Ψ_k Newsletter

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

Number 29 October 1998

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1 Editorial

This Newsletter is over 120 pages long and contains a lot of interesting material. In particular, we would like to turn readers attention to the **General News Section**, where we call for highlight articles for the next year issues of the Psi-k Newsletter. In the **TMR1 Network Section** there is a short report on the *Gd Mini-workshop* that took place last August in Uppsala and one job announcement. In the **TMR2 Network Section** we have one workshop and one job announcement. In the **ESF Programme Section** there are two extensive reports on workshops, partially sponsored by the ESF Programme, both containing abstracts of presented papers. There we also have reports on collaborative visits supported by the ESF Programme. Additionally, two forthcoming workshops are announced in that section. General conference/workshop and job announcements, namely those not sponsored by any of the networks, are to be found in the usual, relevant sections. Moreover, abstracts that are not related to any of the workshops, are in the usual **Abstract Section**. The scientific highlight of this Newsletter on **"Novel reconstruction mechanisms: A comparison between Group-III-Nitrides and "traditional" III-V-Semiconductors"** is by T.K. Zywietz, J. Neugebauer, M. Scheffler and J.E. Northrup. Just before the **Scientific Highlight Section** readers will find some information on CCP3, all-English network, and its biannual newsletter on 'Surface Science'.

For further details readers are kindly asked to check the table of content of the Newsletter.

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

http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

The above contains pointers to home pages of some of the members of our electronic structure community. If you maintain a home page on your activities we will be happy to include a pointer from the *Networks'* home page to your home page.

Please note that the home page of the Psi-k Networks has recently been updated. It contains useful information regarding funding of workshops and collaborative visits within the ESF Programme. Its major new feature is a separate highlight section which contains all highlight articles of the Newsletters published so far.

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

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

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

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

2 General News

2.1 Call for Scientific Highlights for 1999

As the end of the year is fast approaching, we are looking for interesting suggestions for six articles for the **Scientific Highlights Section** of the next year Ψ_k−Newsletters. The first highlight is needed for the February issue of 1999 and would have to be submitted to us about a week before the end of January. The next five issues are: April, June, August, October and December. For those issues the highlight articles need to be submitted about a week before the end of a month preceding the issue month. Concerning the technical side, all highlights need to be written in LaTeX, in the format of the Ψ_k−Newsletters. Also figures, if any, need to be in the LaTeX format, so that the highlight article constitutes a single LaTeX document that can be easily included into the rest of the Newsletter content. We would like to encourage our readers to come forward with suggestions and offers for such articles. Please note that, besides being published in the Newsletter, your highlight article will also feature on a special www-page of the Psi-k Networks (http://www.dl.ac.uk/TCSC/HCM/PSIK/highlights.html), which undoubtedly will increase the exposure of your work. We have three different networks covering many interesting topics some of which have never been presented in the Ψ_k−Newsletters, and this is an excellent opportunity to do so. Moreover, we would also welcome highlights from outside the networks. If any of our readers would like to write a small highlight article, please let us know. We are a very large and lively community and six articles are not so many. Please do contact us with your suggestions as soon as possible.

3 News from the TMR1 Network

"Interface Magnetism"

3.1 Report on Gd mini-workshop

Report on the mini-workshop on
Gadolinium and its f's
in Uppsala, August 19–21, 1998.

A main topic of this mini-workshop was to gather the experience of the advantages and disadvantages of several different approaches to the electronic structure of gadolinium in particular and rare earths in general. Results for calculations treating the $4f$ as valence or core, within ASA or full-potential, within LSDA or GGA, or SIC corrected were presented. A general consensus was that a valent-f treatment seems to give a very good equilibrium volume within GGA while a localized treatment predict a too large volume. However, the former treatment incorrectly obtains an antiferromagnetic ground state while the latter seems to obtain a fairly good energy balance between the ferro- and antiferro-magnetic states. In short, none of these approaches are successful in describing all properties of Gd. Another topic was how to understand the spin-splitting of the valence $5d$ states in Gd that has been observed by different experimental techniques, its temperature dependence and the difference between bulk states and surface states.

The meeting had a very informal character, and not all contributions were presented with an official title. The titles given below is the organizer's own attempt to summarize the contents of the presented talks. About 15–20 persons were present during the seminars and were involved in the sometimes long discussion in-between the talks.

Program of the "Gd" workshop, Uppsala 19–21/8, 1998.

- Leonid Sandratskii, Darmstadt: Band splitting: exchange or spin-mixing?
- Rajeev Ahuja, Uppsala: Ground state properties of Gd.
- Lars Nordström, Uppsala: Magnetic ordering of the heavy rare earths.
- Olle Eriksson, Uppsala: Gd surface with f in core or as valence.
- Alex Mavromaras, Darmstadt: Rare earth superlattices: Gd/Lu, Ho/Lu etc.
- Walter Temmerman, Daresbury: The SIC method and magnetic ordering in Gd.
- Anna Delin, Uppsala: Valence stabilities and equilibrium properties of the rare earths.
- Stefan Blügel, Jülich: The surface states of Gd, where do we stand?
- Börje Johansson, Uppsala: The surface core level shifts of the rare earths.

3.2 Job Announcement

Post-doctoral Position
Condensed Matter Theory
Munich, Germany

Applications are invited from European Union nationals, excluding German residents, for the above position funded by the European Training, Mobility and Research Network on

"Ab-initio Calculations of Magnetic Properties of Surfaces, Interfaces and Multilayers".

The position is available immediately or later in the year for 1 year. There is some chance that this can be extended by a second year. The applicant should not be older than 35 and should have some experience in computational Condensed Matter Theory. She/he is expected to contribute to the current projects of our group in Munich within the mentioned network. This implies that she/he is willing to collaborate with the other members of the network as well. Most of our work deals with spectroscopy, transport and hyperfine interaction dealt with using relativistic multiple scattering theory. Some experience in this area would be helpful but not necessary.

More detailed information concerning the project can be obtained upon request.

Some information on Munich can be found on:

`{\bf http://www.leo.org/leo_e.html}\verb`
`{\bf http://www.munich-online.de/enmunich_online.html}\verb`

Finally and most important: the salary will be around DM 3200.- tax free.

All applications should be sent to:

Prof. Dr. H. Ebert
Institut für Physikalische Chemie
Universität München
Theresienstr. 37-41
D-80333 München
Tel.: (089) 23 94 - 46 42 / - 42 18
Fax.: (089) 28 05 - 248 and (089) 23 94 - 4158
Email: he@gaia.phys.chemie.uni-muenchen.de

4 News from the TMR2 Network

'Electronic Structure calculations of materials properties and processes for industry and basic science'

4.1 Announcement of the Fifth Bristol Workshop

ON THE BOGOLIUBOV-DE GENNES EQUATION FOR SUPERCONDUCTORS

Sponsored by: CCP9 of UK and EU–TMR2 Network

Organised by: **B.L. Györffy and J.F. Annett**

Burwalls, University of Bristol, Bridge Road, Leigh Woods, Bristol, BS8 3PD, UK

November 20 (Friday evening)-November 22 (Sunday lunch), 1998

This workshop is the fifth in the Bogoliubov–de Gennes series of workshops organised in Bristol. This year the following talks are planned. Further details are available from Professor B.L. Györffy at the e-mail address: blg@siva.bris.ac.uk.

Planned Programme

E.K.U. Gross (*Würzburg*)	**Density Functional Theory for Superconductors**
K. Capelle (*San Carlos*)	**Superconductivity and Antiferromagnetism**
C. Lambert (*Lancaster*)	**Phase Coherent Transport in Superconducting Nano Structures**
R. Micnas (*Poznan*)	**Title to be announced**

K. Duncan (*Bristol*)	**A Semi-Classical Theory of the de Haas-van Alphen Effect in Superconductors**
A.S. Alexandrov (*Loughborough*)	**Pseudogaps and Preformed Pairs in the Superconducting Cuprates**
A. Martin (*Geneva*)	**Localization and d-wave Superconductivity**
M. Lüders (*Würzburg*)	**Exchange-Correlation Functional for Superconductors**
K.I. Wysokinski (*Lublin*)	**D-wave Pairing in Disordered Superconductors**
O.K. Andersen (*Stuttgart*)	**Eight-band Models for High T_c Superconductors**
Z. Szotek (*Daresbury*)	**The Quasi-particle Spectrum of $YBa_2Cu_3O_7$ in the Superconductind State**
W.M. Temmerman (*Daresbury*)	**Self-Interaction Corrected LSD for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$**
M. Leadbeater (*Dresden*)	**Title to be announced**
T. Spiller (*Hewlett Packard, Bristol*)	**Quantum Computing**
J.F. Annett, J.J. Hogan-O'Neill (*Bristol*)	**Grain-Boundary Effects in d-wave Superconductors**
J. Wallington (*Bristol*)	**SO(5) Symmetry and the Hubbard Model**

4.2 Job Announcement

INSTITUTE OF PHYSICS AND ASTRONOMY, UNIVERSITY OF AARHUS, DENMARK

Post-doctoral Position

Condensed Matter Theory: Electronic Structure of f-electron materials

Applications are invited for a post-doctoral position funded by the European Training, Mobility and Research Network, **Psi-k**: '*Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Science'* The position is available for a period of 2 years starting first half of 1999. Extension is possible.

The applicant must comply with the TMR rules for network employment of young scientists: The applicant should hold a Ph.D. degree or equivalent in Physics or Chemistry, be younger than 35, and should have some experience in computational Condensed Matter Theory. He/She must be of European Union nationality (or from Norway, Iceland, Israel, or Liechtenstein), however excluding Danish citizens.

The successful applicant shall participate in the network project on investigations of f-electron systems based on the self-interaction corrected version of density functional theory. This implies applications of present computer codes to lanthanide and actinide systems as well as development of improved computer codes. The project is a collaboration in an international team, comprising research groups in Aarhus, Daresbury, Dresden and Uppsala. Some travel activity between the research centers involved must be foreseen. More detailed information concerning the project can be obtained upon request.

The salary depends on seniority as agreed between the Danish Ministry of Finance and the Confederation of Professional Unions.

Applications should include a curriculum vitae, giving evidence on which the evaluation of the applicant's scientific qualifications can be based, a complete list of publications with an indication of those which the applicant selects as the most relevant for the application. The applicant must, upon request, submit further material required by the selection committee in its evaluation.

Applications (4 copies) including two letters of reference should be addressed to: Faculty of Science, University of Aarhus, Ny Munkegade, Building 520, DK-8000

Aarhus C, Denmark, and marked 212/5-139. The deadline for the receipt of all application material is January 15th, 1999.

For further information, contact:

Dr. A. Svane,
Institute of Physics and Astronomy,
University of Aarhus,
Ny Munkegade,
DK-8000 Aarhus, Denmark.
Phone: (+45) 8942-3678,
Fax.: (+45) 8612-0740, Email: svane@dfi.aau.dk.

Information about the Institute can also be found on http://www.dfi.aau.dk.

5 News from the ESF Programme

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

The ESF programme held its inaugural board meeting in Vienna on June 3. At that meeting it was decided to structure this programme in the following interest groups with the following spokespersons:

Methodological Interest Groups

Beyond LDA: *E.K.U.Gross and A. Svane*
f-electrons: *O. Eriksson and H. Eshring*
Plane-wave based techniques: *G. Kresse and J. Neugebauer*
Order(N)+TB: *P. Ordejon and L. Colombo*
FLAPW + other full potential techniques: *S. Blügel and M. Scheffler*
Scattering Techniques (KKR,LMTO): *J. Kollar, H. Dreysse and H. Ebert*

Materials-related Interest Groups

Superconductivity: *B.L. Gyorffy*
Magnetism and magnetic materials: *P. Dederichs*
Surfaces, reactions and catalysis: *M. Scheffler, J. Noerskov, J. Hafner, M. Finnis + industrialist*
Minerals and compounds: *B. Winkler + industrialist*
Alloys: *P. Weinberger and H. Skriver*
Mechanical Properties: *R. Podloucky*
Semiconductors: *R. Nieminen, M. Methfessel and Siemens (Werner)*
Molecular Materials:
Nanostructures and nanotechnologies:
Oxide Materials: *M. Finnis*
Others:

Industrial contacts: *E. Wimmer, J. Hafner, J. Norskov and R. Nieminen*

Some interest groups have no spokesperson and for these we ask for interested people.

The board meeting of the ESF programme will take place in Paris on October 24th. At this meeting, the funding of the ESF workshops for 1999 will be discussed. **If you intend to organize a workshop next year please contact Juergen Hafner (jhafner@tph.tuwien.ac.at) or Walter Temmerman (w.m.temmerman@dl.ac.uk).**

5.1 Announcement of the Workshop on Hydrogen in Semiconductors

To be held at Exeter, UK, April 15-16 April 1999.

Registration will take place on the evening of April 14. The workshop will deal with hydrogen, primarily within Si and at surfaces. Hydrogen in other materials will also be discussed.

The workshop is funded by the European Science Foundation (through the Psik network) and EPSRC through the CCP9 network. It is intended that the workshop will be of interest to both experimentalists and theoreticians, and aims to stimulate collaboration between the two groups.

The main topics of interest will be:

1. Hydrogen–defects including molecules and platelets.
2. Hydrogen–vacancy and interstitial defects.
3. Hydrogen–impurity interactions including transition metals, oxygen and carbon.
4. The smart cut process and other effects of H at surfaces.
5. Hydrogen–oxygen interaction at surfaces.

Other topics may be included.

The workshop is timed to allow participants to travel on to the meeting organised by the European network on defect engineering of advanced semiconductor devices to be held in Greece between the 19th and 24th of April.

Limited funds are available to support participants.

Invited speakers (provisionally) include:

- B. Bech Nielsen (Aarhus, Denmark)
- B. Clerjaud, (Jussieu, France)
- S. K. Estreicher, (Texas Tech, USA)
- L. I. Murin, (Minsk, Belarus)
- R. Newman, (Imperial College, UK)

- A. R. Peaker, (Manchester, UK)
- M. Stavola, (Lehigh, USA)
- K. Stockbro, (MCI, Lyngby, Denmark)
- C. G. Van de Walle, (Xerox, USA)
- G. D. Watkins, (Lehigh, USA)
- J. Weber, (MPI, Stuttgart, Germany)

Further information about the workshop can be obtained from:

R. Jones
School of Physics
University of Exeter
Stocker Road
Exeter EX4 4QL
UK

Telephone +44 1392 264134
Fax: +44 1392 264111
E-mail: `jones@excc.ex.ac.uk`
Dept Office; +44 1392 264151

Workshop URL: http://newton.ex.ac.uk/research/theory/jones/hydrogen/

5.2 Daresbury Workshop Announcement

WORKSHOP ON MATERIALS UNDER PRESSURE

Daresbury Laboratory (UK) **17–18 December 1998**

Supported by CCP9 (Computational Studies of Electronic Structure of Solids)
and ESF Programme STRUC (Electronic Structure Calculations for elucidating the complex
atomistic behaviour of solids and surfaces)

SCOPE

Recent experimenal developments on synchrotrons and neutron facilities have led to much improved structural studies of materials under pressure. Simultaneously, more accuracy in the band structure studies of materials have allowed to explore the crystal structure under pressure in greater detail. The aim of this workshop is to increase the dialogue between experimentalists and theoreticians. The workshop will be primarily concerned with pressure induced structural studies of metals and semiconductors. The final announcement together with the list of speakers will be published in the next newsletter. In the meantime, please feel free to contact the organizers by e-mail: Richard Nelmes (rjn01@rl.ac.uk) or Walter Temmerman (w.m.temmerman@dl.ac.uk).

5.3 Reports on Collaborative Visits

Report on a Short-Time Academic Visit of Dr. A. V. Postnikov (Osnabrück) to IPCMS and Louis Pasteur University, Strasbourg

June 15-20, 1998

The visit was planned for the discussions with Profs. M. Alouani and H. Dreysse on the prospects of our joint effort in the study of electronic structure, magnetic and optical properties of $R\mathrm{NiO}_3$ perovskites (R = rare earth). An interesting feature of these compounds is the metal-insulating transition accompanied by a magnetic transition in temperature. Dr. S. Ostanin also participated in the discussions which took place. We analyzed the experimental information available on the systems in question and discussed the methodological foundations for their efficient first-principles study. The latter must presumable include a reliable structure optimization, with spin-orbit interaction and lifted orbital degeneracy properly taken into account, and be able to provide the information on magnetooptical properties. Relative advantages and disadvantages of the computer codes currently used by our groups came in this respect into consideration.

Since the aspects of local structure instabilities (distortion of oxygen octahedra) are quite important for the $R\mathrm{NiO}_3$ systems as well as for perovskites in general, I presented in some detail the results obtained in our group in Osnabrück within last years in what regards the first-principles study of ferroelectric perovskites. During my stay, I gave three lectures for the academic staff at the IPCMS and the students of the Louis Pasteur University on:

“Theoretical Aspects of Ferroelectricity in Perovskites”,
“LDA+U Calculations for Perovskites” and
“Macroscopic Polarization and Density-Polarization Functional Theory”.

Andrei Postnikov

Report on a visit by S.S.A. Razee (Warwick, UK) to Prof. P. Weinberger's group (Vienna, Austria)

August 2-13, 1998

I am a post-doctoral Research Fellow with Dr. J.B. Staunton at the University of Warwick, Coventry (UK) working on the magnetic anisotropy of thin films and multilayers using spin-polarised relativistic screened KKR-CPA method. I visited Computational Materials Science group (Prof. P. Weinberger and his group) at the Institut für Technische Elektrochemie, Technische Universität Wien (Austria) under the ESF Scientific Programme on "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces (STRUC-Ψ_k)" from August 2, 1998 to August 13, 1998. In Vienna I worked closely with Dr. Laszlo Szunyogh who is one of the architect of the screened KKR method, and along with Dr. B. Ujfalussy, has developed the screened KKR code for surfaces and multilayers. In our project we plan to use this code as an starting point and develop it to study more complex properties such as finite temperature magnetism in thin films. During my stay at Vienna I learnt the structure and technical details of the existing screened KKR code and also its running. Also, during this time, we incorporated the CPA for the substrate as well as cap materials in this code and in the code for the magnetic anisotropy. Now these codes are applicable to pure as well as disordered bulk solids, their surfaces, interfaces, thin films and multilayers alike.

The knowledge which I gained about the structure of the code and its technical details, will obviously help me greatly when I set up the appropriate codes for the finite temperature studies within the disordered local moments (DLM) picture, the paramagnetic susceptibility, and the effect of atomic short-range order on the magnetocrystalline anisotropy energy (MAE). Also, since we have access to the Cray-T3D machine at EPCC we would like to parallelise the code. These programs would have been impossible without a good knowledge of the structure and working modes of the existing code. While I am developing the codes for the above studies, we plan to calculate the MAE of thin films as well as surfaces of alloys of Co and Pt. This will complement our earlier work on bulk CoPt alloys and other solids. We have already started these calculations at Warwick (UK). On the whole this was a very useful visit and would help me gretaly in pursuit of our project. Besides, it has helped us setting up an important collaboration with the group at Vienna. We hope to have several publications together in near future.

The computer codes which will come out of this collaborative program will also be useful to other electronic structure theorists working in this area and will be made available via CCP-9 and European networks.

Report on a Collaborative Visit of A. Zupan (Ljubljana) to the Technical University of Vienna in Austria

August 9 - August 12, 1998

I visited Dr. Peter Blaha at the Technical University of Vienna, from August 9 to August 12, 1998. This visit enabled a continuation of our collaboration, which started in 1997. We worked together in the field of the Density Functional Theory. We mainly tested the behavior of new gradient-enhanced exchange-correlation functionals in solids and explained the impact of the gradient correction on the calculated transition pressure in the pressure induced phase transitions.

During this visit, we worked on two different issues:

- We implemented two versions (TH1, TH2) of the empirical Tozer-Handy exchange-correlation functional and potential into the FP-LAPW code WIEN. This functional makes a step forward from old B3LYP or B3PW91 empirical functionals since it uses accurate numerical exchange-correlation potentials in the fitting procedure and takes into account the integer derivative discontinuity in the energy. Though, the first preliminary results are not very encouraging. The lattice parameter of silicon is overestimated by 10 %, magnetization of iron is far too large (2.8 μ_B instead of 2.1 μ_B). We expect some better results for other include molecules with heavier atoms (transition metals) into the training set.
- We implemented the local kinetic energy into the code. This required a fairly big modification of the code (LAPW0 and LAPW2). The local kinetic energy $\tau(\vec{r}) = \sum_i \frac{1}{2}|\nabla\varphi_i(\vec{r})|^2$ is a novel ingredient of a exchange-correlation functional that is currently being developed by J.P. Perdew and his collaborators. First results are quite promising, the lattice constant of silicon, which is by 2% too long in the PBE approximation, is very close to the experimental value.

This has been a very fruitful visit, the planed work was completed in 3 days instead of proposed 5. We expect to have publications of this work submitted by the end of this year.

5.4 Reports on Workshops

5.4.1 Report on Workshop in Sardinia

Report on the VIII Workshop on Computational Materials Science held 18 to 22 September 1996 in S. Margherita di Pula, (Cagliari), Sardinia, Italy

The eight edition of the Workshop on Computational Materials Science [formerly known as Computational Condensed Matter (1990-1994) Italian-Swiss (1990-1997) Workshop] was held on the south-western coast of Sardinia, Italy from 18 to 22 September. The main sponsors were Regione Autonoma Sardegna (the regional government of Sardinia) and the Ψ_k European Science Foundation Network; UNESCO bestowed its prestigious patronage. About 40 participants gathered at the Workshop, in a pleasant location and in an informal atmosphere, also favored by the nice weather. Social and scientific programs blended together nicely, favoring intense discussion and contacts.

The focus of this workshops series has traditionally been electronic structure problems, mainly attacked by means of ab initio density-functional methods. Also ab initio molecular dynamics and less-common topics such as polarization theory have been well represented in past editions. While keeping to a large extent in track with the tradition of past meetings, this edition has devoted considerable attention to semiempirical and model approaches, to statistical mechanics, and to experiment. While this necessarily implies (given the sum rule on the workshop length) that the cross section of each single topic is somewhat smaller than usual, this program formula has had the definite merit of bringing in “fresh blood” in the form of new (or hitherto unfamiliar) concepts and viewpoints, besides the obviously necessary confrontation with inputs from experimental activity. Attempting a somewhat arbitrary classification, out of 18 one-hour invited talks there were 8 ab initio ones, 3 experimental, 4 on semiempirical, classical, and analytical methods, and 3 on statistical mechanics. Wide-ranging applications were discussed in all cases.

Ab initio studies focused on polymers (Andreoni, Barkema), fullerenes (Andreoni) metal/nonmetal transitions in liquids (Hafner), on complex events in defects and bulk diffusion (Jonsson, Barkema), on surface diffusion (Jonsson) and molecular dissociation and reactions (Hafner), and on charge density waves in adsorbate systems (Santoro). In these talks, considerable emphasis was put on the search for minimum energy paths in diffusion and dissociation events, and two main methods (the nudged elastic band and the activation relaxation technique) were discussed. Among the problems touched upon, let us mention new mechanisms for Si self-diffusion, water molecules diffusing on ice, CO oxidation and thyophene de-sulfurization at the surfaces of catalysts, and defect restructuring in glasses.

Semiempirical and classical dynamics methods and models were applied to tight binding semiconductor device simulation (Di Carlo), phase transitions in adsorbate layers (Persson), polymer fracture (Persson), and sliding friction (Persson). Device simulation with tight binding proved capable of interpreting complex situations such as optical amplification in heterostructure systems, and the anomalies of the laser effect in wurtzite nitrides due to macroscopic polarization;

thereby ab initio predictions on polarizations and simulations were nicely coupled. The other talks proved in a very compelling way that deep physical intuition and carefully designed, but simple calculations can be efficiently elucidate complex issues in "real-materials-science" problems such as friction and fracture.

Statistical mechanics talks dealt with the fascinating notion of self-organized criticality (Vespignani), tackled from both the theoretical, simulational, and experimental point of view. An exciting application of these seemingly exotic methods to the motion of magnetic domain walls and the Barkhausen effect in ferromagnetic alloys (Zapperi) demonstrated how knowledge from such far-afield areas as the statistical mechanics of self-organization can be brought to bear on practical problems in materials science. The "smart" simulation of De Gennes polymer reptation (Barkema) drew on statistical mechanics as well as on advanced numerics and intensive computation.

The experimental talks dealt with superconductor-semiconductor devices (Beltram) and STM (Rieder). In the former talk, the observation of Andreev reflection from a semiconductor was reported. The possibility of engineering transport across the semiconductor-superconductor junction by means of local dipole alterations was also demonstrated. In the latter two talks, technologically relevant and physically exciting uses of the STM were demonstrated in complex nanoengineering and restructuring of surfaces and the observation of surface charge density waves.

In the about 15 posters presented in a very lively evening session, the relative weigths of the different topics reflected largely those in the lectures. The issues touched upon were diverse: to mention some, molecular polymeric materials, percolation modeling of electrical fatigue in devices, non-quasiparticle behavior at surfaces (experimental), chaos in laterally confined superlattices in magnetic fields, thermal expansion of and adsorption on metal surfaces, semiconductor alloys, etcetera.

The abstract of the lectures, and the list of posters follows below.

INVITED TALKS

Towards Long-Time Simulations of Disordered Materials

Gerard Barkema

Computational Physics, Faculty of Applied Physics, Technische Universiteit Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Microscropic structural phenomena in disordered materials often proceed on time scales remarkably long compared to those of the atomistic oscillations. This prohibits numerical studies with the traditional method, molecular dynamics (MD). In some areas where the building blocks of the dynamics are particularly well-known, e.g. surface science, it has been possible to reach long time-scales in atomistic simulations by means of event-based simulation techniques. This talk will discuss how such event-based simulation techniques can also be used for the simulation of disordered materials, by means of the Activation-Relaxation Technique (ART). Some results will be presented for a-Si, a-GaAs, silica, and metallic glasses.

Simulation of models for polymer reptation

Gerard Barkema

Computational Physics, Faculty of Applied Physics, Technische Universiteit Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands

In 1971, de Gennes has introduced the concept of "reptation": movement of a polymer by means of diffusion of stored length. To obtain insight in the scaling behaviour of reptation, two lattice polymer models are widely studied: de Gennes' model for polymer reptation, and Rubinstein's repton model. For both models, it is hard to obtain high-quality simulation data, due to the long correlation times involved with long poymers. In this talk, both models will be discussed, including efficient ways to simulate these. The most accurate simulation results to date will be presented, and their physical relevance discussed.

Some results on advanced semiconductor "devices"

Fabio Beltram

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Today's experimental research on semicondutor micro and nanostructures opens up many issues demanding nontrivial modelling. In this talk I shall present some recent experimental results of the experimental condensed matter group at Scuola Normale Superiore that point at open questions requiring structural-, electronic- or optical-property calculations.

The first case study will be that of engineered semiconductor-superconductor junctions. I shall present our data for the InGaAs/Al junction both above and under crytical temperature for the case of native and modified junctions. The latter are realized by inserting Si monolayers at the interface under proper growth conditions. Achievement of ideal ohmic junctions and Andreev-reflection dominated transport will be shown.

Additionally I shall show results on InAs/Nb junctions again pointing at Andreev dominated transport and to the role of the surface condition in determining the junction transparency.

For the case of semiconductor heterostructures, based on transport measurements, I shall argue that the above-mentioned Si-interlayer scheme is not applicable owing to Si diffusion during semiconductor growth. I shall finally present some results on magnetotransport in periodic heterostructures that indicate the need for an adequate description of electron-hole interaction in the Zener process. For the intraband case the need for a quantitative description of the interplay between in-plane magnetic field and heterostructure potential will be discussed.

Tight-binding methods applied to semiconductor nanostructures and devices.

Aldo Di Carlo

INFM-Dipartimento di Ingegneria Elettronica, Università di Roma "Tor Vergata"

Electronic and optical properties of semiconductor nanostructures based on homo- and heterojunctions have been investigated theoretically by means of a variety of tools. The empirical tight binding method (TB) has been shown to be a valid alternative to commonly used approaches based on the envelope function approximation (EFA), since it improves the physical content without requiring a much higher computational effort. Indeed, TB allows us to account for band nonparabolicity, valence band mixing as well as thin layer perturbations, overcoming the natural limitations of the EFA formalism. Moreover, we have recently shown [1] that TB methods can be implemented in a self-consistent fashion in order to account for charge redistribution.

As a first application of the TB method, results concerning electron transport in pseudomorphic high electron mobility transistor (P-HEMT) will be presented. Here the use of strained InGaAs quantum well is responsible for carrier confinement in the HEMT channel. We have applied the tight-binding model coupled with a Monte Carlo simulator and calculated the electroluminescence emitted by the P-HEMT in the pre-breakdown conditions. The theoretical results compare well with available experimental spectral. We show how the braking of InGaAs symmetry in the channel of the P-HEMT induces optical transition nominally symmetry-forbidden. In a second example, the tight-binding method has been used to calculate the polarization dependence of delta-strained InP/InGaAs semiconductors optical amplifiers (SOA) [2]. We explain how thin strained GaAs layers embedded in a lattice-matched InGaAsP/InGaAs quantum well can be used to achieve polarization insensitive optical amplification. Finally, we show how TB can be used to study spontaneous [3] and piezoelectric polarization effects in nitride-based devices. We show how self-consistency should be considered to properly describe the screening of the polarization field due to the free charge.

The tight binding method can be also applied to nanostructures where the electrons are confined in one-dimension, namely T- and V-shaped quantum wires (QWR) [4]. The large hamiltonian matrix which results from the realistic dimensions of the unit cell (more than 10000 atoms), has been diagonalized by using a generalization of the Lanczos algorithm without reorthogonalization. This analysis of QWR shows that band mixing between wire Γ states and barrier X states can drastically change the electronic properties of the conduction band.

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Large-scale ab-initio molecular-dynamics calculations: Applications to fluid metals and alloys close to a metal-insulator transition

Jürgen Hafner

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The basic principles of the Vienna ab-initio simulation program VASP for performing large-scale ab-initio density-functional molecular-dynamics simulations for metallic systems are reviewed. Applications to metals and alloys close to a metal/nonmetal transition are described. The examples chosen range from expanded fluid mercury to hot molten selenium to Zintl-alloys formed by alkalis and polyvalent elements showing salt-like order or polyanionic clustering at critical compositions.

Ab-initio simulation of reactions at solid surfaces

Jürgen Hafner

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With the first ab-initio modelling studies of catalytic reactions becoming available, we are now well underway towards a quantum mechanics of catalysis. In this contribution, ab-initio studies of two catalytic reactions of industrial relevance are described: (a) The oxidation of carbonmonoxide on the platinum (111) surface and (b) the hydrodesulfurization of thiophene on transition-metal–sulfide surfaces.

The NEB method for Finding Minimum Energy Paths and Application to Si Bulk Self-diffusion

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A typical atomic scale transition, for example a chemical reaction, or a diffusion event in a crystal, involves a significant activation barrier and as a result such transitions occur on a much longer (many orders of magnitude!) timescale than the time interval over which atomic dynamics can be simulated on a computer, even when empirical interaction potentials are used. As a result, direct dynamical simulations are largely ineffective for finding unknown transition mechanisms in large, complex systems. By use of transition state theory (TST), an estimate of the transition rate can be obtained given the minimum energy path (MEP) of the transition. The maximum energy along the MEP gives the activation energy barrier, a central quantity in the harmic approximation to TST. The practical problem becomes to find what the final state of the system will be after the transition, and to find the MEP between given initial and final states. A robust method called the Nudged Elastic Band method for finding the MEP will be discussed. An application of the method to the study of Si self diffision in Si crystal using DFT/LDA description of the atomic interactions will also be presented. Several minimum energy paths for the diffusion of interstitials as well as the path for concerted exchange of pairs of Si atoms have been determined and the activation energy compared with measurements of the diffusivity.

Adsorption, diffusion, and island formation of water molecules on the surface of proton disordered ice

Hannes Jonnson

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Theoretical calculations of the deposition, adsorption, diffusion, and island formation of water admolecules on the basal face of ice Ih will be presented. The calculations are based on both pairwise additive interaction potentials as well as a polarizable model. The modeling of the electrostatic interactions between water molecules will be discussed and results of the induction model compared with DFT calculations. The sticking coefficient is found to be near unity for water vapor deposition, but drops to 0.9 for incident energy of 1.5 eV and 60 degree angle of incidence. At low coverage, an admolecule prefers to sit at non-crystallographic sites (i.e. not fitting into the ice lattice) with a large binding energy. Since ice Ih is proton disordered, there is a range of binding energies, and for some local environments the binding energy is on the order of (and even larger than) the cohesive energy. The proton disorder also results in a range of activation energies for diffusion. After mapping out a large number of diffusion barriers using accelerated dynamics and the Nudged Elastic Band method, a kinetic Monte Carlo calculation of the diffusion at 140 K was performed. At short time, the mean squared displacement has anomalous scaling with time as is common for diffusion on random lattices. From the long time scaling a diffusion barrier is obtained which is not inconsistent with recent upper bound found by Brown and George. The simulated diffusion is also reasonably consistent with earlier estimates of the diffusion length by Mason. Paths and energy barriers for the formation of small islands have also been studied. It is found that islands up to and including pentamer are non-crystallographic, but the hexamer is crystallographic. The dominant activation energy barrier to the formation of a new crystallographic island is the admolecule diffusion barrier.

Ordered Structures and Phase Transitions in Adsorbate Layers

B.N.J. Persson

IFF, Forschungszentrum Jülich, Germany

In discuss the nature of ordered structures and phase transitions in adsorbed layers. I treat both order-disorder transitions and the properties of incommensurate structures. Result of numerical simulations based on molecular dynamics and the Monte Carlo method is presented and compared with experimental data [1].

1. B.N.J. Persson, Surface Science Reports **15**, Nos. 1-3 (1992).

Physics of Sliding Friction

B.N.J. Persson

IFF, Forschungszentrum Jülich, Germany

I present a broad overview of sliding friction with emphasize on results obtained during the last few years. I present results of computer simulations which indicate that boundary lubrication involves dynamical phase transitions in molecularly thin lubrication layers [1]. The relative importance of electronic and phononic friction on metal surfaces is discussed in relation to recent measurements of the sliding friction on a superconducting substrate.

1. B.N.J. Persson: Sliding Friction, Physical Principles and Applications (Springer, Heidelberg, 1998).

Model Study of Brittle Fracture of Polymers

B.N.J. Persson
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I present a model study of brittle fracture of polymers. I show that the relation $\mathbf{v} = \mathbf{v}(\mathbf{F})$ between the crack-tip velocity $\mathbf{v}$ and the driving force $\mathbf{F}$ exhibit discontinuous transitions and hysteresis. For short polymers, at the onset of crack-propagation the polymer chains separate by pulling out the molecular chains, while a discontinuous transition to a new state of rapid crack motion occur at higher driving force, where the polymer chains break. In contrast to earlier atomistic studies of crack motion involving brittle materials such as silicon, for short polymers we find (at zero temperature) that the onset of crack-motion is continuous, i.e., the crack-tip velocity $\mathbf{v}$ increases continuously from zero when $\mathbf{F}$ is increased above the critical value necessary for starting crack motion. The difference is attributed to inertia, which is less important during pullout of the molecular chains, than in models where the crack motion involves breaking strong short-ranged bonds. I also present a detailed study of the polymer chain pullout process.

Surface Structuring with the STM

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One possible future way to create new materials and devices consists in the atom by atom assembling of functional structures on solid substrates. The instrument with which manipulations on atomic scale became possible is the scanning tunneling microscope [1, 2]. The two basic modes of the transport of atoms or molecules to form proper patterns consist of picking up the particles with the tip and releasing them back to the surface at the desired places (vertical manipulation) or to move them along the surface maintaining contact to the substrate (lateral manipulation). For a secure control of both transfer modes the basic physical steps involved in both manipulation modes have to be known.

We report on recent studies of lateral transfer of Pb- and Cu-atoms and CO-mole-cules on Cu(211), which allowed us to distinguish repulsive (pushing) as well as continuous (sliding) and discontinuous (pulling) attractive manipulation modes [3]. On Cu(111) in the case of pulling of Cu-atoms even finer details can be discerned: the adparticle may show various movement patterns visiting different surface sites upon applying different tip forces [4].

A very important further development concerns lateral manipulation of native sub-strate atoms: On Cu(211) we could show that atoms at sixfold coordinated kink sites and even sevenfold coordined sites at regular step edges can be released and used for atom by atom build-up of prototypic structures, whereby also deeper sub-strate layers may be included [5].

Vertical manipulation has been proven up to now for Xe-atoms as well as propen- and CO-molecules [6]. Detailed investigations concerning the ultrafast electronic mechanism behind the controlled vertical manipulation of CO-molecules are re-ported [7]. Vertical manipulation implies the important consequence of creating functionalized tips, which are structurally and compositionally well defined. For STM imaging this may lead to chemical sensitivity and improved resolution [8].

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Charge density effects visualized with STM

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Scanning Tunneling Microscopy (STM) as well as with Atomic Force Microscopy (AFM) and by Atom Beam Diffraction (ABD). Whereas - to reasonable approximations - the corrugations of both AFM and ABD are related to density contours of the total charge density, STM operated at low voltages filters out the contributions near the Fermi level. Therefore STM is especially sensitive to charge density waves as well as electron states localized at metal surfaces. Examples for both charge density waves (CDW) in layered compounds as well as surface electron states confined in differently shaped "corrals" are presented. In layered materials the electric field between tip and sample can give rise to local phase transformations with other CDW periodicities. Employing various tip-sample interactions like forces and/or fields layered materials may also be modified down to atomic scale; this leads to the fascinating possibility to shape their CDW properties in dependence of manmade defect arrangements. For ABD it is shown, that for He "anticorrugating effects" can falsify the image of close packed metal rows, whereas Ne yields the correct picture; this effect can be traced back to the different electronic structures of He and Ne.

Surface charge density waves and Mott insulators for adlayer structures on semiconductors

Giuseppe Santoro,[1,2] **Sandro Scandolo**,[1,2] and **Erio Tosatti**[1,2,3]
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[3] *International Center for Theoretical Physics (ICTP), Strada Costiera, Trieste, Italy*

Motivated by the recent experimental evidence of commensurate surface CDW in Pb/Ge(111) and Sn/Ge(111) $\sqrt{3}$-adlayer structures, as well as by the insulating states found on K/Si(111):B and SiC(0001), we have investigated the role of electron-electron interactions, and also of electron-phonon coupling, on the narrow surface state band originating from the dangling bond orbitals of the adsorbate. We model the problem by an extended two-dimensional Hubbard model at half-filling on a triangular lattice. The hopping integrals are calculated by fitting first-principle results for the surface band. We include an on-site Hubbard repulsion U and a nearest-neighbor Coulomb interaction V, plus a long-ranged Coulomb tail. The electron-phonon interaction is treated in the deformation potential approximation. We have explored the phase diagram of the model including the possibility of commensurate 3×3 phases, using mainly the Hartree-Fock approximation. For U larger than the bandwidth we find magnetic insulators, possibly corresponding to the situation on the SiC and in K/Si surfaces.For smaller U, the inter-site repulsion V can stabilize metallic CDW phases, reminiscent of the 3×3 structures of Sn/Ge, and possibly of Pb/Ge. Comparison with available first-principle calculations is made.

Avalanche Processes in Collective Transport Phenomena

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Avalanches are common in many nonequilibrium systems involving energy or matter transfer and are often distributed as a power law, indicating an underlying critical behavior. Driving fields, random inhomogeneities and dissipative effects play a central role in understanding and classifying these phenomena. We analyze various possible scenarios giving rise to avalanche dynamics. Relations with the general scaling picture present in many experiments are discussed. Focusing on the simple class of Self-Organized Critical models we discuss how the wide time-scale separation in nonlinear dynamical systems becomes a general mechanisms for the generation of avalanches.

New perspectives for the Barkhausen effect

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The precise connections between the Barkhausen effect and non-equilibrium critical phenomena and self-organized criticality have been strongly debated in the past few years. We review the recent theoretical studies of the Barkhausen effect and discuss their relevance to quantitatively understand the experiments. We compare the results of disordered spin models, micromagnetic equations, and models for rigid and flexible domain walls with experiments on amorphous and polycrystalline ferromagnetic alloys. In particular, we discuss the theoretical predictions for the critical exponents of the power-law decay and for the cutoff of the avalanche distributions. We conclude that models based on the dynamics of a flexible domain wall are the most successful in explaining existing experimental data.

POSTERS

A Theoretical Study of the Structure and Lattice Dynamics of Semiconductor Surfaces with Adsorbates: An Application to Si(001), Marcus Arnold, Pasquale Pavone, and Ulrich Schröder, Theoretische Physik, Universität Regensburg, Germany

Structural Properties and Quasiparticle Energies of Cubic SrO and MgO, Giancarlo Cappellini,[1] F. Finocchi,[2] S. Bouette-Russo,[2] and C. Noguera,[2] 1) INFM – Università di Cagliari, Cagliari, Italy, 2) LPS, Université Paris-Sud, France

An All-atom Force Field for the Simulation of Dynamics and Structures of a class of Cromophores in a Photosynthetic Reaction Center, Matteo Ceccarelli, Piero Procacci, and Massimo Marchi, CECAM, Ecole Normale Superieure Lyon, France

Electronic Properties of Porphyrin Molecular Stacks, Fabio Della Sala,[1] Aldo Di Carlo,[1] Paolo Lugli,[1] Fabio Bernardini,[2] Vincenzo Fiorentini,[2] Corrado Di Natale,[3] Arnaldo D'Amico,[3] and Roberto Paolesse,[4] 1) INFM-Electronic Engineering, University of Rome "Tor Vergata", 2) INFM-Department of Physics, University of Cagliari , 3) Department of Electronic Engineering, University of Rome "Tor Vergata", 4) Department of Chemistry, University of Rome "Tor Vergata"

Interaction of Oxygen with Rh(111) Surfaces, M.V. Ganduglia-Pirovano and M. Scheffler, Fritz-Haber-Institut der Max-Planck Gesellschaft, Berlin, Germany

Electron-lattice interaction on α-Ga(010), Ph. Hofmann,* Y.Q. Cai,* Ch. Grütter,+ and J.H. Bilgram+ * Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, and Institute for Storage Ring Facilities, Aarhus Universitet, + Laboratorium für Festkörperphysik, ETH Zürich

Vibrational Dynamics and Thermodynamics of Metallic Nanocrystals, Abdelkader Kara and Talat S. Rahman Kansas State University, Manhattan, KS 66506, USA

Ab-initio study of Be (0001) surface thermal expansion, Michele Lazzeri and Stefano de Gironcoli, INFM-SISSA, Trieste, Italy

Representing high-dimensional *ab initio* potential-energy surfaces with neural networks, S. Lorenz, A. Groß, and M. Scheffler Fritz-Haber-Institut, Berlin, Germany

Structure and Phase Stability of Wide Gap II-VI $Be_{1-x}Mg_xSe$, $Be_{1-x}Zn_xSe$ and $Mg_{1-x}Zn_xSe$ Alloys, Stefano Martinelli and Stefano de Gironcoli, INFM - SISSA, Trieste, Italy

Nonadiabatic Fragmentation of Excited Molecular Ions: an Exploratory Study for N_2H^+, G. Materzanini[1] and F.A.Gianturco[2] 1) Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Italy, 2) Dipartimento di Chimica, Università di Roma "La Sapienza", Roma, Italy

$SOCl_2$, SO_2Cl_2: Energy Dispersive X-ray Diffraction, ab-initio and molecular Dynamic calculations, S. Meloni, A. Pieretti, L. Bencivenni, V. Rossi Albertini,* C. Sadun, and R. Caminiti INFM – Dipartimento di Chimica, Universitá "La Sapienza", Roma, Italy, * Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Frascati, Italy

Electrical Instability of Thin Films Driven by Joule Heating, Cecilia Pennetta,[1] and L. Reggiani[2] , 1) INFM-Dipartimento di Fisica, Università di Lecce, Italy, 2) INFM-Dipartimento di Scienza dei Materiali, Università di Lecce, Italy

First-Principles Study of Raman Intensities in Semiconductors, Bernhard Steininger, Pasquale Pavone, and Dieter Strauch Theoretische Physik, Universität Regensburg, Germany

Magnetism on rough overlayers - an augmented space recursive study, Biplab Sanyal, S.N.Bose National Center for Basic Sciences, Calcutta, India

Chaotic dynamics in LSSL heterojunctions, F. Meloni, R. Tonelli, G. Santoboni,* and S. Sanna, INFM – Dipartimento di Fisica, Università di Cagliari, (*) Centre for Nonlinear Dynamics, University College London, UK

5.4.2 Report on CECAM Workshop

LOCAL ORBITAL METHODS FOR LARGE SCALE ATOMISTIC SIMULATIONS

Sponsored by

CECAM

ESF Programme on "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces" (Psi-k)

Universidad Autónoma de Madrid and Universidad de Oviedo

22-25 July 1998

Lyon, France

The workshop was held at CECAM in Lyon (France), from July 22 to July 25 1998. It was organized by Pablo Ordejón (Universidad de Oviedo), Luis Seijo (Universidad Autónoma de Madrid), Giulia Galli (LLNL) and David Pettifor (University of Oxford). It was organized in the CECAM style, with 30 invited speakers, and 16 other scientists attending the workshop. There were 30 oral talks given by the invited speakers, and a session with posters presented by other participants. The workshop was intended to be a forum for discussion, and therefore plenty of time after each talk and at focused discussion sessions was available.

The main goal of the workshop was to evaluate the present status of local orbital bases for electronic structure-based atomistic simulations. These techniques are having an important boost in the last years due to the high efficiency and accuracy that they can attain. Part of this renewed interest is due to the recent development of Order-N techniques, which find their natural language in the context of local orbital bases. Besides, local orbitals are being widely used in several communities, including condensed matter physics, materials science, quantum chemistry and biochemistry, although the interaction between them is not always as good as it would be desirable. An important objective was to bring these communities together, and it seems to have been a key factor for the success of the workshop. In particular, the contact between the quantum chemistry and the solid state communities probed particularly fruitful, with a very lively exchange of fresh points of view during the workshop discussions.

The workshop was organized around seven Sessions. In most of the Sessions there was a long review talk (to give the general frame and context to the session), and a few other short invited talks. The Sessions were the following:

1. Empirical Tight-Binding Parametrizations

   B. Koiler gave a review talk on the subject covering the most important ideas of the TB method, and showing applications in two classical problems in semiconductor physics: the variation of the gap in random alloys and the energetics of defects. *C. Z. Wang* and *M. Menon* discussed about alternative schemes for reliable environment dependent TB parametrizationss. Finally, *H. Polatoglou* described the calculation of optical properties within the TB formalism, and parametrizations for obtaining reliable results.

2. Tight-Binding Applications

   Turchi, Colombo, Kaxiras and *Kim* described applications of the TB method to large scale materials problems, like stability of multi-component metallic alloys, disordered covalent systems and extended defects. *Oleinik* described the Bond-Order Potentials method, and its application to metals and covalent systems.

3. Approximate Density Functional Theory and Semiempirical Methods

   W. Yang described recent attempts to apply semiempirical quantum chemistry methods (in combination to Order-N techniques) to the study of biological systems. *Sankey* reported a recent experience in building an approximate DFT code (Fireballs) in the context of a University-Industry collaboration. *Drabold* described several applications of approximate DFT to disordered systems. *Elstner* discussed the extension of approximate DFT to include charge selfconsistency effects, and reported results in several systems ranging from organic molecules to semiconductor surfaces and defects. *Flores* described an alternative approach to DFT (which in principle includes significant correlation effects), in which the orbital occupations (instead of the charge density) are the basic variables of the calculation.

4. Density Functional Theory with Local Orbital Bases

   Delley reviewed the use of numerical basis sets for DFT calculations, and analyzed the issues of numerical integration and achivement of O(N) scaling. This was also the goal of the presentation of *Hutter*, but with a method based on Gaussian wave functions. *Bowler* described recent advances towards O(N) DFT using real space grids, where the "localised support functions" defining the density matrix are optimized.

5. Quantum Chemistry Methods

   Bagus gave a review on quantum chemistry ideas for analysis of electronic structure information, which may help in identifying the mechanisms that lead to the observed properties. *Dovesi* described the Crystal program for HF and DFT calculations in crystals. *Malrieu* and *Stoll* discussed about the direct calculation of Wannier functions in solids, and their use in determining the correlation energy. *Carter* analyzed strategies to reduce the scaling of Configuration Interaction calculations, based on the ideas of localization and in pseudospectral methods. These methods promise to make CI calculations available for relatively large systems in the near future.

6. First Principles Order-N Calculations

   Artacho discussed the Siesta approach for O(N)-DFT calculations within the LCAO approach. He stressed the neccessity of finite range bases for efficiency, and described ways to optimize the new types of basis sets to achieve maximum accuracy. *Scuseria* described the issues in achieving linear scaling with Gaussian basis sets, stressing those concerning the calculation of the Hamiltonian matrix elements. *Stechel* discused several concepts related to linear scaling-linear response calculations.

7. Other Non-Standard Localized Basis Sets

   Vanderbilt started the last Session addressing the calculation of optimally localized Wannier functions, which are relevant for many of the subjects covered by the workshop. *Martin* described recent advances in the use of wavelets for electronic structure, *Annett* discussed the possibility of mixing real space grids with atomic or localized orbitals, and *Haynes* described the use of localized spherical waves. Finally, *van Shilfgaarde* discussed the generation of minimal basis sets from LMTO calculations, and a technique to compute efficiently the electronic structure of layered materials.

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Empirical Tight-Binding methods for the electronic properties of semiconductors

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The Tight-Binding (TB) approximation was originally proposed by Bloch [1] and was examined in full detail by Slater and Koster [2] for the electronic spectrum in a periodic potential. This scheme has since been continually adopted both as a tool for qualitative or semi-quantitative understanding of electronic density of states [3,4] and as a powerful method with predictive reliability for electronic and structural properties of solids [5].

Because of its simplicity, the TB approach is particularly appealing for the treatment of inhomogeneous and disordered solids. The lack of periodicity may be dealt with by adopting large cells with periodic boundary conditions. Finite-size effects are usually dealt with by increasing the cell size and examining the convergence of the desired properties. In some situations, however, this is not practical or necessary, and accurate extrapolation to infinite-cell size is possible. As an illustration, we will discuss two classical problems in semiconductor physics, for which finite size effects may be completely eliminated through appropriate scaling techniques. The first problem concerns the direct-to-indirect crossover in AlGaAs random alloys. In analogy with temperature-driven first-order phase transitions, we perform a systematic study of the scaling of calculated gap properties with cell size, and find that they follow scaling laws appropriate for first-order phase transitions. Extrapolation to infinite system size allows an accurate determination of the crossover composition [6]. The second problem concerns impurity states in semiconductors. The proposed TB treatment for the binding energy of a single substitutional impurity is valid for shallow as well as deep levels [7], but is expected to be most useful for intermediate levels for which conventional approaches break down. In spite of the long-range nature of the perturbation Coulomb potential, we obtain a practically perfect fit for an exponential convergence of the binding energy. The scaling regime is attained for cells above a minimum size which depends on the depth of the impurity level, and for Ge acceptor impurities in GaAs requires cells with at least 4096 atoms.

The TB approach has also proven valuable in the study of semiconductor heterostructures, particularly for narrow quantum wells or short-period superlattices, when atomistic effects become relevant [8]. Realistic profiles of the interfaces may be incorporated in fully real-space TB calculations. In particular, atomic interdiffusion [9], segregation [10] and interface roughness [11] effects in the optical properties of quantum wells have been investigated through large cells TB calculations.

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Environment-dependent Tight-Binding potential model*

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Generating accurate and transferable tight-binding potentials for molecular dynamics simulation of realistic materials is an outstanding challenge. Traditionally, tight-binding potentials are constructed using the two-center approximation for the tight-binding hopping parameters formulated by Slater and Koster more than four decades ago [1]. While the two-center approximation greatly simplify the TB parametrization, neglecting multi-center interactions is justified only when the electrons are well localized in strong covalent bonds. For systems where metallic effects are significant in addition to the covalent bonds, the two-center approximation becomes inadequate.

Recently, we have developed a new generation of tight-binding model which goes beyond the traditional two-center approximation and allow the tight-binding interactions to be dependent on the bonding environment [2-4].

In our model, the environment dependence of the tight-binding parameters are modeled through incorporating two empirical scaling functions into the traditional two-center integrals. The first one is a screening function which mimics the electronic screening effects in solid such that the interaction strength between two atoms in the solid becomes weaker if there are intervening atoms located between them. This new approach allows us to distinguish between first and farther neighbor interactions within the same interaction potential without having to specify separate interactions for first and second neighbors. The second function scales the distance between two atoms according to their effective coordination numbers. Longer effective bond lengths are assumed for higher coordinated atoms. The strength of the hopping parameters between atoms i and j are therefore dependent on the coordination number of the atoms: weaker interaction strength for larger-coordinated structures. This new model preserves the two-center form of the tight-binding hopping integral while the multi-center effects are taking into account.

Based on this model, we have generated environment tight-binding potentials for carbon, silicon, germanium, aluminum and molybdenum. The cohesive energies as a function of nearest neighbour distance for these materials in different crystalline structures obtained from the present tight-binding potentials agree well with the first-principles calculation results. The potentials also describe well the phonon frequencies and elastic constants in these materials in comparison with experiments. Our fitting results indicate that the present environment-dependent tight-binding model has good transferability to describe not only the lower coordinated covalent structures, but also the higher coordinated metallic materials.

In addition to the properties of the bulk crystalline structures, we have performed extensive tight-binding molecular dynamics simulation to evaluate the accuracy and transferability of the potentials for describing more complex systems. The systems that we have studied include the structures of medium-sized silicon clusters (Si_{11} to Si_{20}), defects and diffusion on the Si(111)-(7x7), adatom and addimer diffusion on the Si(100), silicon grain boundaries, structure and dynamics of diamond surfaces, and the reconstruction of Mo(100). Our studies show that these potentials are very useful in predicting the structures and properties of the complex systems.

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Generalized Tight-Binding molecular dynamics for real materials

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Virtually all properties of solids and molecules are determined by their electronic structure. Although *ab initio* techniques for the determination of electronic structure have existed for many decades, utilizing these to determine atomic dynamics has begun only relatively recently with the advent of large-scale computing. Unfortunately, the computational complexity and memory requirements of these methods have forced the application to be limited to relatively small supercell sizes. It is clear that while simulations based on classical potentials can be useful in situations where no major chemical or electronic rearrangements take place, the study of chemical reactions, interfacial growth, surface chemisorption, etc. requires explicit treatment of the valence electrons.

Thus, a semi-empirical bridge between *ab initio* computations on the one hand, and classical potential simulations on the other is highly desirable. Recently, Menon and Subbaswamy introduced a minimal parameter tight-binding scheme suitable for molecular dynamics simulations of covalent systems [1,2,3] .The method differs from the conventional tight-binding methods in that explicit use of non-orthogonality of the basis is made in the formalism. This allows for proper accounting of the local coordination information in the electronic structure Hamiltonian, resulting in excellent transferability for structural and vibrational properties of Si from dimer through bulk with only a minimal number of adjustable parameters.

Application of the formalism to small Si clusters in the range up to N=10 gave excellent agreement with *ab initio* results [4,5] for structures, cohesive energies and frequencies. When applied to the bulk phases of Si, GTBMD has reproduced binding energy differences between the high-pressure metallic phases and the diamond phase in excellent agreement with the schemes based on the local density approximation (LDA) [3]. Furthermore, the GTBMD scheme predicts clathrate phases to be higher in energy when compared with the diamond phase. This is important when one considers the fact that most conventional orthogonal schemes, while giving good results for the higher density phases of Si (β-tin, simple cubic, and fcc), predict the clathrate phase to be the ground state, in disagreement with LDA results and experiment [6,7].

We have recently examined the structural and vibrational properties of the lowest energy clathrates [7]; specifically a clathrate structure containing 34 atoms in a face-centered cubic (fcc) unit cell and another structure containing 46 atoms in a simple-cubic (sc) unit cell, using our generalized tight-binding molecular dynamics (GTBMD) scheme. We also obtained the Raman spectra for these crystals within a bond polarizability model. The vibrational spectra reported for both clathrates are obtained, for the first time, using quantum methods and contain many interesting features, the most striking being the presence of a gap.

Applications of the nonorthogonal tight-binding molecular dynamics method to carbon systems have also been met with success. The nonorthogonal scheme has been found to be very reliable in obtaining good agreement with experimental and local density approximation (LDA) results for the structural and vibrational properties of fullerenes and nanotubes [8,9].

Electronic structure analysis shows that carbon nanotubes can be either metallic or semiconducting, depending on both the diameter and chirality. Carbon nanoscale junctions can be created by connecting dissimilar nanotubes with components that can be either metallic or semiconducting. This leads to the exciting possibility of synthesizing nanoscale devices with these junctions forming the building blocks. We recently proposed the geometric structures of complex junctions made of these nanotubes that are of interest to experimentalists. Three-point (5,5)-(10,0)-(5,5) junction (Fig. 1) has been found to be a local minima of our molecular dynamics scheme and could be the building blocks of nanoscale tunnel junctions in a 2D network of nanoelectronic devices [10]. The structural and electronic properties of a variety of interconnects have been investigated using the present scheme. The local densities of states (LDOS) that provide valuable insights into the device properties have also been studied using a Green's function method.

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Figure 1. GTBMD relaxed (5,5)-(10,0)-(5,5) junction. Dark balls denote the atoms forming the heptagons. The structure contains six heptagons and no pentagons. (PostScript file available upon request; email to ordejon@condmat01.geol.uniovi.es)

Tight-binding extension of ab-initio results to study the optical properties and the thermodynamics of complex systems

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Recently a great effort has been placed on the approximate solution of the electronic problem of large systems. To this effort we try to contribute working on two major directions. We use the semiempirical tight-binding approach tackling the problem of optical properties of semiconductor systems and thermodynamics of intermetallic compounds and alloys. We are going to present some of our results on both directions.

By making a three-center up to third-neighbor tight-binding fit to the electronic structure of Si and Ge it is shown that not only the electronic structure of both, the conduction and valence bands can be reproduced, but also interesting optical properties like the dielectric function and the absorption spectra can be calculated with an accuracy comparable to state-of-art calculations. In this way it is possible to study economically the optical properties of large semiconductor systems.

In this direction we will present examples of the detailed study of the optical properties of Si/Ge superlattices (finite and periodic), hydrogen-terminated Si-quantum wires related to porous Si, Si-quantum wires embedded in Ge and Ge-quantum wires embedded in Si. A rich variety of behavior is observed, which cannot be described by simple models and may be of relevance for optoelectronic applications.

In the other direction the tight-binding theory in the second moment approximation is also used to produce an N-body potential determined from the T=0 K bulk properties (lattice constant, cohesive energy and the elastic properties of Cu, Au and Cu_3Au), in order to study some macroscopical and microscopical properties of bulk Cu_3Au, CuAu and $CuAu_3$, as well as twisted, tilted and antiphase boundaries and surfaces, performing Monte Carlo simulations, at temperatures below and above the transition temperature. Our findings reproduce the bulk order-disorder transition and compare well with known experimental results. An interesting point is that also properties of the other Cu-Au compounds and alloys can be described satisfactory using the potential which was fitted to the bulk properties of Cu_3Au.

Studying the effect of the boundaries and the surface on the ordering of Cu_3Au we concentrated our investigation on segregation and wetting phenomena taking into account relaxations of the atoms. We found no segregation of either Au or Cu to the interfaces, but found that Au segregates to the surface. On the other hand we observed wetting of the boundary by the disordered state only for the interfaces. The interfaces and surfaces act as a disordering force, with very interesting consequences.

Extended recursion and its application to stability in complex materials

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The aim of this presentation is to review some of the recent progress made in the field of alloy theory, with reference to the mathematical theory of orthogonal polynomials and continued fractions which both formally describe the real-space extended recursion method [1,2] and its application to the calculation of the one-electron Green function. For simplicity sake, the formalism relies on a realistic tight-binding (TB) model Hamiltonian for the description of the electronic properties, although at a later stage of development a more accurate charge self-consistent electronic structure method could be used.

Most physical properties exhibited by multi-component alloys are driven by the existence of specific chemical long-range order as functions of temperature and concentration, a reason why alloys based upon simple underlying crystalline structures have received much attention in recent years [3,4]. On the contrary, very few studies have been undertaken on fundamental grounds to investigate *the interplay between topological disorder and chemical short-range order*, and their impact on properties and design, in alloys with reduced symmetry, such as in the presence of defects (interface, surface, grain boundary, dislocation, etc.), or in the absence of any symmetry, as in the case of amorphous materials.

When dealing with the atomistic description of chemical order in alloys, one has to combine electronic structure calculations with a statistical treatment, both requiring a high degree of accuracy. One way to meet this challenge is to cast the quantum mechanical description of the energetics of an alloy in an Ising form which is most appropriate for a subsequent statistical mechanics treatment of order-disorder phenomena as functions of temperature and concentration [4]. The mapping of the energetics resulting from the solution of a suitable electronic Hamiltonian onto an Ising form has been originally achieved within the so-called generalized perturbation method (GPM) [3], which is a pertubative way of accounting for the fluctuations of local concentration in a reference medium which is as close as possible to any chemical configuration of the alloy. Such suitable medium is given by the chemically disordered state, as described within the coherent potential approximation (CPA) [3,5]. Subsequently, the method has been generalized to account for chemical correlations inside finite clusters embedded in the CPA-reference medium, thus leading to the so-called embedded cluster method (ECM) [6]. In both methods, only the configuration-dependent contribution to the total energy is expressed by an expansion in terms of effective multi-site interactions, and since the reference medium is concentration-dependent, so are these interactions. Within the ECM, the configurational (or ordering) energy for a binary alloy is given by

$$\Delta E_{\mathrm{ord}}(\{\delta c_n\}) = \sum_n h_n \delta c_n + \sum_{n,m\neq n} V_{nm}\delta c_n \delta c_m + \cdots$$

where δc_n refers to the fluctuation of concentration on site n, $\delta c_n = p_n - c$, where c is the concentration in B-species, and p_n is an occupation number associated with site n, equal to 1 or 0 depending on whether or not site n is occupied by a B-species. The h_n are the effective on-site energies which act as chemical potentials. Because of the properties of the reference medium, an expansion up to two-body interactions is usually enough to provide the required accuracy. The effective pair interaction V_{nm} between sites n and m is given by the expression: $V_{nm} = V_{nm}^{\mathrm{AA}} + V_{nm}^{\mathrm{BB}} - 2V_{nm}^{\mathrm{AB}}$, which indicates that if its sign is positive, it favors the formation of an AB-pair (tendency towards ordering), otherwise it favors the formation of an AA or a BB pair (tendency towards clustering).

Once these interactions are known, the set of all possible ordered states which are stable at zero-temperature and at particular concentrations, can be predicted. Finally, combined with Monte Carlo (MC) simulations, the configurational part of the free energy can be computed, and hence, phase stability properties can be summarized as functions of temperature and concentration [4].

As said before, most studies on stability and order have been performed so far for alloys based on simple periodic lattices. To extend such methodology to alloys based on complex lattices in the presence of extended defects, as well as to topologically (structurally) disordered materials, one has to devise efficient algorithms to, first, solve the CPA equations in the case of an inhomogeneous system, and second, obtain the effective interactions which will build up the configurational part of the total energy. The energetics information can then be used with canonical MC simulations (Kawasaki dynamics) to predict the chemical configuration of a given alloy. The lattice on which the alloy is based is then relaxed with tight-binding molecular dynamics (TB-MD) simulations. The different time scales which are commonly involved are now taken care of within a consistent electronic structure framework (here, TB), *i.e.*, MD solves the short time scale issues (vibrations and relaxations) and MC solves the long time scale problems of atomic diffusion and atomic rearrangement of species, and therefore both chemical and topological disorders are treated on the same footing. With this new scheme we hope to solve the problems encountered in current studies in which the structural part of the problem is usually addressed with empirical potentials (such as Lennard-Jones or Morse) prior to defining the electronic structure properties of the system [7,8]. We will show that the localized recursion basis is ideally suited for solving the CPA equations [9] in the case of an inhomogeneous system, and for extracting with an orbital peeling technique [10] the energetics which is required to perform MC simulations.

Finally, it is worth noting that the global scheme is applicable to the study of a wide class of problems, among others: (i) the inclusion of vibrational energy and entropy, and the energy due to the relaxation of the lattice in the calculation of the total Gibbs energy for the construction of phase diagrams; (ii) the study of alloys in the liquid or the amorphous state; (iii) reconstruction, relaxation, ordering and concentration profile for alloys in the presence of surfaces; (iv) diffusion at interfaces in bulk and multi-layered materials; (v) the more general phenomenon of nucleation and growth in alloys.

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From point to extended defects in silicon: TBMD investigation on nanocavities and small self–interstitial clusters

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The National Technology Roadmap for Semiconductors [1] is, at present, the most widely cited strategic plan for semiconductor industry. In that document, among the highlights for future development of Si–based microelectronics, a special role is reserved to atomistic simulations: in fact, any projection for further technological improvements clearly indicates that we will need a very good physical understanding and a very good modelling capability for microstructural evolution of silicon under various processing steps.

The above scenario defines an interesting playground for large–scale tight–binding molecular dynamics (TBMD) simulations. As a matter of fact, TBMD (although implemented at the semi–empirical level, with an orthogonal and minimal basis set) can provide the accuracy needed to describe, at the relevant length– and time–scale, the evolution of the directional and covalent Si–Si bond during native defects migration and interaction [2].

In this talk I will review some recent investigations on the formation, binding, and chemical properties of vacancy clusters (i.e. nanocavities) [3] and rod–like structures (i.e. self–interstitial clusters) [4] originated by the coalescence of point defects. These complexes represent, respectively, the intermediate step for microdefect formation in Czochralski crystal growth and one of the various features affecting post–implantation phenomena (like, for istance, crystal–to–amorphous transition, formation of planar defects, defect–mediated mass transport).

Our computational framework consists in a hierarchy of codes, ranging from model–potential molecular dynamics (MPMD) to TBMD. While MPMD is used for exploratory simulations and pre–processing of structures, O(N) TBMD [5] is extensively adopted to anneal and fully relax the defect complexes, as well as to investigate their finite–temperature stability. Finally, TBMD (based on the standard diagonalization of the tight–binding matrix, but parallelized through a SMP library [4]) is used to compute the energetics of formation and binding.

Furthermore, in order to study electronic properties, we have extended our investigation beyond the semi–empirical TBMD level. The atomic coordination and bond structure of the defect complexes have been solved by means of an electron–density topological analysis within the quantum theory of atoms in molecules (QTAM). In order to perform QTAM, we computed the electron wavefunction through a Restricted Hartree–Fock calculation performed, in turn, on the TBMD–generated configurations [6].

As for self–interstitial clusters, we show that small complexes give rise to three–dimensional structures where the local atomic coordination increases monotonically with cluster size. At variance, larger clusters exhibit a spontaneous trend to self–organization which drives the system to rod–like defects. As for nanocavities, we show that different growth patterns exist and that an interplay between energy and topology arguments determines the most stable aggregates.

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Development and applications of empirical and semi-empirical methods to the study of disordered covalent systems

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The study of the atomic structure, dynamical evolution, and electronic properties of disordered systems through simulations has become an important complement to experimental observation. Such simulations need to include large numbers of atoms and must cover substantial time intervals to capture the atomic processes that are responsible for macroscopic phenomena. At present, this can be accomplished efficiently only with empirical and semi-empirical methods. We will discuss our recent efforts to develop empirical and semi-empirical methods that describe faithfully atomistic processes in covalent materials, which is a challenge due to the strong directional bonding and localized nature of the interactions. We will also discuss certain applications of these methods to disordered (amorphous) phases and their interfaces with crystalline phases. Both in the method development part and in the applications we will focus on silicon as the representative covalent solid.

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Molecular dynamics simulation of large scale Si and C systems using a tight-binding $O(N)$ method

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We have developed a linear scaling method ($O(N)$) for electronic structure calculations and molecular dynamics simulations based on an orbital formulation [1]. We report applications of the orbital based $O(N)$ method to large scale carbon and silicon systems in tight-binding representations: (i) We study structural properties and energetics of the extended {311} defects that contain interstitials [2] and their stabilities at high temperatures; (ii) We simulate the deposition of C_{28} clusters on a semiconducting surface and the growth of disordered C_{28} solids by cluster collisions [3]. We also discuss works in progress to simulate long-time-scale dynamics, such as diffusion of interstitial chains in bulk Si, with no significant increase in computational time.

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Bond-Order Potentials: bridging the electronic-atomistic length scale gap

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The atomistic modelling of materials involves research across the broad range of length scales. At the electronic level the Schrödinger equation is solved to predict electronic states and energies. However, even with the biggest supercomputer only about 1000 atoms can be treated from first principles, so that the maximum size of the unit cell is of the order of nanometers. In order to simulate larger systems, the electronic degrees of freedom must be removed through the use of interatomic potentials. This allows the modelling of up to about one thousand million atoms on the largest supercomputers, so that the atomistic hierarchy extends to the order of tenths of microns.

Obviously, there exist a gap between the electronic and atomistic modelling hierarchies in the sense that large-scale *atomistic* simulations based on interatomic potentials are often notoriously unreliable because they have removed the electronic degrees of freedom which small-scale *ab initio* computations at the *electronic* level treat correctly. Besides, the time required to solve the Schrödinger equation at the electronic level scales as the cube of the number of atoms in the unit cell, i.e. it is an $O(N^3)$ problem or at best $O(N^2 lnN)$. Solving the Schrödinger equation to find the eigenvalues and eigenfunctions is treating the problem *globally*, since a small perturbation in any region of the cell effects the eigenfunctions everywhere throughout the cell. On the other hand, the use of finite-range interatomic potentials in metals and semiconductors reduces the simulations to a linear $O(N)$ problem, since a change in one region of the cell will not affect the properties in a distant region of the cell, i.e. the problem is being treated *locally.*

Atomistic simulations of the behaviour of real materials, however, can only be as reliable as the interatomic potential used to model the interactions between the atoms. Although there have been dramatic developments during the past decade with the advent of embedded-atom-type potentials for metals [1, 2] and bond-order potentials for semiconductors [3, 4], the applicability of these potentials beyond the narrow confines of the fcc noble metals and sp^3-bonding situations, respectively, remains questionable. There is, thus, a need to bridge the gap between the electronic level with its solution of the Schrödinger equation and the atomistic level with its use of interatomic potentials.

In principle, this gap between the electronic and atomistic hierarchies may be bridged for systems which are well described by the Tight-Binding (TB) approximation. This approximation is quantitative for sp-valent systems such as the hydrocarbons and semiconductors but it is more qualitative for the d-valent metals. Within the TB approximation the energy of any given bond may be written as the product of the bond integral and the bond order, where the bond order gives the difference between the number of electrons per spin in the bonding state compared to the antibonding state.

It has been shown that the bond order can be expressed as an exact many-atom expansion in terms of the local atomic environment about the bond [5-7]. For angularly-independent s-valent orbitals the first term in this so-called bond-order potential (BOP) expansion is reminiscent of the second-moment approximation to the local density of states that was used by Finnis and Sinclair [2] for the atomistic modelling of metals. For angularly-dependent orbitals which overlap to give rise to a s bond the first term in the BOP expansion is very similar to that proposed by Tersoff [3] for the atomistic modelling of semiconductors. However, we will show that the second-moment approximation is unable to account for the well-known structural trends within the periodic table. In this talk we shall briefly review the theory of the BOPs, their place in the hierarchy of other order of N methods based on tight binding and discuss recent developments in analytic BOPs.

Very recently, we have used the BOP formalism to four levels to derive a simple analytic expressions for the bond order of σ and π bonds [8]. It has been shown to provide a reliable model for carbon and silicon which allows structural differentiation between different crystal phases of Si and C, see the figure (PostScript file available upon request; email ordejon@condmat01.geol.uniovi.es). We are currently developing this model to include the case of nonzero s-p atomic energy level separation. In the latter case, in addition to the pairwise repulsive and many-body bond terms the promotion energy contribution is also naturally appeared in the BOP formalism and provides very important ingredient to describe the chemistry and physics of covalent systems in various environments. The application of BOP for constructing analytic potentials for hydrocarbons will also been considered.

We will also review recent advances in BOPs applications for metals [9]. In spite of the great popularity of embedded atom method (EAM) [1] and many-body potentials of the Finnis-Sinclair type [2] in studies of metallic materials, their success in applications to bcc and hcp transition metals was limited. In this case, the BOP method provides valuable order of N alternative since it includes explicitly the covalent component of bonding. It is well known that in transition metals the relative stability of alternate crystal structures is controlled by the level of of the filling of the d-band. Consequently, covalent bonding mediated by the d electrons plays a significant role in determination of low-energy structures of extended lattice defects. We will illustrate the features of the bond order potentials in application to the hcp Ti [9]. Important ingredient of the BOP formalism for the studies of metals is the introduction of the fictitious electronic temperature to damp down the long-range Friedel oscillations and to achieve rapid real-space convergence. The examples of BOPs calculations include the studies of stacking-fault type defects and stability of the hcp structure with respect to large homogeneous deformations and alternative structures [9].

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Linear scaling methods and applications to biological systems

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We have developed a divide-and-conquer linear-scaling method for quantum mechanical simulation of large biological systems. Solvent effects are described with a continuum dielectric model. It has been applied to the determination of solvation free energies, charge distribution and electrostatic potential surfaces of protein and DNA systems at the semiempirical level. The aqueous polarization effects on the electronic structure and thermodynamic properties of macromolecules will be presented. Recent applications on the study of active species for the ground-state complex of cytidine deaminase and the electronic structure of the proteins and DNAs will be described. The method presented here extends the realm of quantum chemical techniques to applications of macromolecular systems in solution.

We will also present the development and applications of absolute energy minimum principles for linear scaling quantum mechanical calculations, and our progress on linear-scaling first principle approaches.

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Recent developments using Fireball orbitals and the Fireballs-2000 project

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The use of fireball orbitals and approximate DFT methods using them has been around for about 10 years now. During June and July of 1998, an “experiment” will be performed in which a team of researchers will be assembled from universities and industry with diverse interests to completely redo the codes we use, and construct a more user friendly and versatile methodology and code. This project has been named Fireballs-2000, and the work will immediately precede the conference. We will describe what was accomplished, as well as failures, and the difficulties that we faced. An issue of relevance to the "code-producing" community is how well and efficient such an "extended group" can function, particularly in the short but well-defined time frame that industry demands.

Tight-Binding and approximate density functional studies of disordered systems

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In this talk, I discuss several applications of local basis techniques ranging from empirical tight-binding to fully *ab initio* local basis density functional methods. I concentrate on disordered insulators, which I argue are ideally suited to local orbital methods and will benefit particularly from order-N methods. Two examples will be considered:

Lanczos + tight-binding [1]: the Anderson transition in amorphous silicon. Using a highly realistic 4096 atom model of a-Si [2], I discuss the qualitative character of the electronic eigenstates as a function of energy from midgap (where they are strongly localized) well past the mobility edge (where they are extended), and from this calculation a simple picture of the localized to extended transition emerges [3].

Fireball [4] + Siesta [5]: The properties of liquid and glassy $GeSe_2$. Long time scales, large supercells and transferability are *required* to form and analyze models of amorphous and glassy systems. We [6] have recently published models of disordered phases of $GeSe_2$ in close agreement with known experimental properties. The Harris functional LDA methods of Sankey [7] were used. We comment on recent work [8] concerning *why* GGA corrections are important in plane wave LDA calculations on the GeSe system, using SIESTA and Car-Parrinello methods [9].

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Selfconsistent-charge density-functional tight-binding methodology for simulations of complex materials properties

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THEORETICAL METHOD

We focus on describing in detail the systematic extension of the tight-binding formalism and of our DFTB scheme [1] in order to derive a generalized selfconsistent charge (SCC) methodology and to improve total energies, forces, and transferability. This differs from previous approaches since we base the modification of the TB total energy expression on a strict second-order expansion of the *Kohn-Sham* energy functional with respect to density fluctuations at a given reference density [2]. The new methodology ensures a proper distribution of the charge and overcomes the requirement of local charge neutrality, especially in multi-component systems. In maintaining the simple two-center picture of the non-SCC standard DFTB, the new scheme can be easily incorporated into any standard TB-method.

The zero-th order approach is equivalent to a common standard non-selfconsistent (TB) scheme. Employing the *Mulliken* analysis for the transferred charges the approximate second order DFT total energy is conveniently transformed into a transparent TB expression. Finally, a variational minimization of the approximate 2-nd order functional within an LCAO framework yields a transparent, parameter-free, and readily calculable expression for generalized Hamiltonian matrix elements. These are determined by a selfconsistent redistribution of *Mulliken*-charges (SCC). In addition to the usual "band-structure" and short-range repulsive terms, the final approximate *Kohn-Sham* energy includes a *Coulomb*-interaction between charge fluctuations. At large distances this accounts for long-range electrostatic forces between two point-charges and approximately includes self-interaction contributions of a given atom if the charges are located at one and the same atom. We apply the new SCC-scheme to problems where deficiencies within the non-SCC standard TB-approach become obvious. We demonstrate the improvements considering properties of molecular, biological and solid state systems.

RESULTS

In order to validate the SCC-DFTB approach we are presenting results of first successful applications of the SCC-DFTB scheme to a wide class of systems which are of interest in chemistry, physics and biology.

Organic molecules

For our first benchmark, we have calculated the reaction energies of 36 processes between small closed shell molecules containing oxygen, nitrogen, carbon, and hydrogen [3]. We have found a mean absolute deviation from experiment of 8.8 kcal/mol for the SCC-DFTB, compared to 11.1 kcal/mol for DFT-LSD and 4.6 kcal/mol for DFT-GGA calculations. Further, considering the optimized geometries of a 63 organic molecules test set [4], the mean absolute deviations from experiment in the bond lenghts and bond angles are $\Delta R = 0.012\AA$ and $\Delta\theta = 1.7^\circ$ [2] respectively, compared to $\Delta R = 0.017\AA$ and $\Delta\theta = 2.0^\circ$ by using the semi-empirical AM1 Method [4].

The improvement over the non-SCC treatment is impressively demonstrated for systems with a delicate counterbalance between ionic and covalent bonding contributions, as e.g. in formamide. The DFTB method overestimates the equalization of single and double bonds in the amide and carboxyl groups. This is exclusively due to too much charge flow (of nearly one electron) from carbon to oxygen, clearly indicating the need for a selfconsistent charge redistribution. SCC can considerably improve vibrational frequencies of simple molecules, like for example CO_2, in which a wrong charge transfer crucially affects force constants. As in the formamid molecule a too, large charge transfer from carbon to oxygen is obtained, connected with an underestimation of the CO bond strength. The symmetric and antisymmetric stretching modes ($\sum_g$ & $\sum_u$) in CO_2 change from 1458 & 1849 cm^{-1} in DFTB to 1348 & 2305 cm^{-1} in SCC-DFTB in good agreement with the experimental values, 1333 & 2349 cm^{-1}. Frequencies have further been tested for a series of 33 (O, N, C, and H)-containig molecules from Ref. [5] yielding 6 % mean absolute deviation of vibrational frequencies from the experiment [2].

Biological systems

The very promising results for the organic molecules described above lead us to believe that the method can be applied to investigate the geometric and electronic structure of large biomolecules. We focus only on some examples, where semi-empirical methods are known to have defficiencies. We have simulated the retinal in the bacteriorhodopsin molecule, a polyene structure linked via a Schiff base to the protein matrix. The SCC-DFTB geometries are in good agreement with the experimentally reported crystalline structure of the retinal [6]. In particular, the planar relaxation of the retinal Schiff base is correctly described, a characteristic which both classical force field and semiempirical calculations have failed to reproduce. Another important property for a realistic simulation of structural and energetic properties of peptides and proteins is the rotational barrier in formamide. This is largely underestimated by semiempirical methods so that it is usual to correct for the associated effects by empirical force fields. In contrast, the SCC-DFTB barrier height is in good agreement with the experiments deviating by only 10 %. This leads to a reliable description of the energetics and structure of different conformers of small polypeptides.

Since DFT-LDA is known to perform poorly for H-bonded systems, one has to go beyond this level of description. One natural extension is provided by the use of gradient-corrected functionals such as the PBE-GGA [7]. By applying this functional in both the full SCF reference calculations and the construction of the TB Hamiltonian (GGA-atoms and matrix calculations by superposition of densities) [2], the effects of hydrogen bonding within the SCC-DFTB may be described at a corresponding level of accuracy. For example, for the water dimer the linear structure is found to be the global minimum and the O..O distance is underestimated by 4 % with respect to the experimental value, which is comparable to the performance of DFT-GGA methods. In order to test the SCC-DFTB for these systems systematically, we calculated the bonding energies of 18 weak and strong hydrogen-bonded compounds and studied barriers for proton transfer in cationic and anionic systems [2]. Although some well know deficiencies of DFT-GGA calculations (concerning the underestimation of proton barriers) cannot be overcome, the overall description is reliable yielding a clear improvement compared to semi-empirical AM1 and PM3 Hamitonians. A detailed study of H-bonded DNA base pairs will presented elsewhere.

III-V semiconductor surfaces and defects

Within the SCC-DFTB we calculated structures and formation energies for GaAs and GaN surfaces [2] and showed that deficiencies of standard DF-TB can be removed yielding a very good agreement with recent SCF-LDA plane wave calculations [8,9]. We then applied the SCC-DFTB scheme to GaN threading screw and edge dislocations modeled in large clusters and supercells containing 576 atoms [10] and found that these line defects are electrically inactive, i.e. they do not exhibit deep gap states. Nevertheless, parasitic yellow luminescence (YL) is observed in strong correlation with such line defects. Point defects like the Ga-vacancy, oxygen and related complexes which have previously been suggested to make a large contribution to the YL band in GaN are found to be particularly stable at the core of the threading edge dislocation where oxygen sits two-fold in a brigde position [11].

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A LCAO-OO approach to the calculation of electronic properties of molecules and solids

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A selfconsistent LCAO approach for describing the properties of molecules and solids is presented. The basic many-body LCAO-hamiltonian is calculated using an atomic-like wavefunction basis, $\psi_\alpha(\vec{r} - \vec{R}_i)$, and introducing the Löwdin's orthogonal basis :

$$\phi_\mu = \sum_\nu (\mathbf{S}^{-\frac{1}{2}})_{\mu\nu}\psi_\nu. \tag{1}$$

where $(\mathbf{S})_{\mu\nu} =< \phi_\mu|\phi_\nu >$, and $\nu \equiv (i, \alpha)$ defines the orbital α at the site i.

In this orthogonal basis, the LCAO-hamiltonian is written as follows:

$$\hat{\mathcal{H}} = \sum_{\nu,\sigma} \epsilon_\nu \hat{n}_{\nu,\sigma} + \sum_{\sigma,\mu\neq\nu} t_{\mu\nu}\hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} + \sum_{\nu\omega\sigma\mu\lambda\sigma'} O^{\nu\mu}_{\omega\lambda}\hat{c}^\dagger_{\nu\sigma}\hat{c}^\dagger_{\mu\sigma'}\hat{c}_{\lambda\sigma'}\hat{c}_{\omega\sigma} \tag{2}$$

In a first step, core levels of hamiltonian (2) are replaced by a new LCAO pseudopotential that is calculated using a second order expansion in the overlap $S_{c\nu}$ between the core, c, and the valence, ν, orbitals. Introducing the pseudopotential components, $V^{ps}_{\nu\nu}$ and $V^{ps}_{\nu\mu}$, we can define the following valence electron hamiltonian:

$$\hat{\mathcal{H}} = \sum_{\nu\sigma}(\epsilon_\nu + V^{ps}_{\nu\nu})\hat{n}_{\nu\sigma} + \sum_{\nu\neq\mu,\sigma}[t_{\nu\mu} + V^{ps}_{\nu\mu} + \sum_{\lambda,\sigma'} h_{\lambda,\nu\mu} n_{\lambda\sigma'} - \sum_{\lambda} h^{x}_{\lambda,\nu\mu} n_{\lambda\sigma}]\hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\mu\sigma} \tag{3}$$

$$+ \sum_{\nu} U_\nu \hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow} + \frac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}(J_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu\bar{\sigma}} + (J_{\nu\mu} - J^{x}_{\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}) \tag{4}$$

In eqn. (3),

$$V^{ps}_{\nu\nu} = \sum_{c} S_{\nu c}S_{c\nu}(E - E^{0}_{c}) + \sum_{c} J^{0}_{\nu c}(n_{c\uparrow} + n_{c\downarrow}) + \sum_{c}[J^{0}_{\nu c}(S_{\nu c})^{2} - J^{x,0}_{\nu c}]n_{c\sigma} \tag{5}$$

$$V^{ps}_{\nu\mu} = \sum_{c} S_{\nu c}S_{c\mu}(E - E^{0}_{c}) + \sum_{c} h^{0}_{c,\nu\mu}(n_{c\uparrow} + n_{c\downarrow}) + \sum_{c}[\frac{J^{0}_{\nu c}J^{0}_{\mu c}}{2}S_{\nu c}S_{c\mu} - h^{x,0}_{c,\nu\mu}]n_{c\sigma} \tag{6}$$

Integrals U, J, J^x, h, h^x refer to different Coulomb interactions for either Löwdin's (U, J, J^x, h, h^x) or atomic (U^0, J^0, $J^{x,0}$, h^0, $h^{x,0}$) orbitals. These integrals are calculated using conventional quantum chemistry codes.

In a second step, we analyze the many-body terms of hamiltonian (3) using an orbital-occupancy (OO) approach. In this approach, the orbital occupation numbers, $n_{\nu\sigma}$, plays the same role the electron density $n(\vec{r})$ does in conventional LD approaches. This allows us to introduce the many-body energy $E^{m.b.}[n_{1\sigma}, n_{2\sigma}, ...]$ associated with hamiltonian (3). Moreover, by introducing the local potential

$$V^{m.b.}_{\nu\sigma} = \frac{\partial E^{m.b.}}{\partial n_{\nu\sigma}} \tag{7}$$

we can substitute hamiltonian (3) for the effective one-electron hamiltonian:

$$\hat{\mathcal{H}}^{eff} = \sum_{\nu\sigma}(\epsilon_\nu + V^{ps}_{\nu\nu} + V^{m.b.}_{\nu\sigma})\hat{n}_{\nu\sigma} + \sum_{\nu\neq\mu,\sigma}[t_{\nu\mu} + V^{ps}_{\nu\mu} + \sum_{\lambda,\sigma'} h_{\lambda,\nu\mu} n_{\lambda\sigma'} - \sum_{\lambda} h^{x}_{\lambda,\nu\mu} n_{\lambda\sigma}]\hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\mu\sigma} \tag{8}$$

This one-electron hamiltonian is solved and the occupation numbers, $n_{\nu\sigma}$, are obtained selfconsistently. Then, the total energy is calculated as done in conventional LD-methods.

We stress that the main difficulty in applying this approach appears in the calculation of $E^{m.b.}[n_{1\sigma}, n_{2\sigma}, ...]$. We shall present our approximated $E^{m.b.}[n_{1\sigma}, n_{2\sigma}, ...]$ by splitting it into the Hartree, exchange and correlation contributions. We shall show that the limit of high correlation is well-described by our method, making it suitable for analyzing highly correlated systems.

We shall present results for different molecules, H_2O, CH_4, ... and solids, Si, C and NiO.

DMol^3: numerical atomic-response basis sets and tricks for larger scale full DFT calculations

B. Delley

The broad applicability to a wide variety of compound types of density functional approximations made it obvious in the 80's that such atomistic calculations might be useful for industrial research on electronic properties of potentially useful compounds. When Dmol finally got released in 88/89, it probably was the first commercially available DFT program. Very soon, usefulness of DFT predictions for fluorine compounds were demonstrated by Dave Dixon.

Already in its first version Dmol featured a very robust basis set available readily for the entire periodic system. The idea got finally published in the method paper [1]. A lesson was learned from the linearized augmented plane wave (LAPW) method, which still today is considered a reference method for solid state DFT calculations. Inside the atomic spheres just two functions per angular momentum channel, a regular radial function at some mean band energy and a derivative function, are used to span the variational function space. This was adapted to molecular problems by using a numerical function set for the free atom, plus appropriate 'derivative' functions. Functions for higher angular momentum, as derivatives with respect nonsperical fields, are clearly important for accurate molecular calculations, and are part of the normal basis set. We call this double numerical plus polarization (DNP) basis set. Contrary to the LAPW these numerical functions are allowed to overlap in the spirit of an LCAO method. The convergence as a function of angular momentum is helped very much by allowing overlap instead of ℓ expansion inside each muffin tin sphere. The limit of spin-restricted separated atoms is handled with an accuracy comparable to that of numeric atomic programs. With the relatively small standard set of atomic plus 'derivative' functions the exact solution is approached to milihartree accuracy for spin polarized atoms, non-sperical atoms and molecular bonds [1]. In retrospect one may see the Dmol basis set as a numerical implementation of atomic response basis sets [2]. Cutting the (numeric) atomic tails to finite length has been investigated by Sankey and Niklewski [3]. For a general purpose basis set we prefer to use more conservative higher cutoff radii.

The numerical atomic response basis sets appear not to allow analytical integration even for overlap matrix elements. This may seem to be a decisive disadvantage, but, at least the more complicated density functionals require numerical integration of matrix elements anyway. Ref [1] describes a partitioning method to reduce the global integrations to a sum of quasi atomic integrations. These site integrals are done as radial-angular product integrations. Typically, the angular integrations use Lebedev rules; a recent review, including extension for higher orders and more accurate parameters for the integration rules can be found in [4]. A numerical integration has the interesting property that the computational effort can go down with decreasing overlap of the basis functions. Long before the fock and overlap matrices become sparse, the effort to calculate them can turn into the linear scaling regime.

Electrostatic potentials and potential matrix elements for the continuous densities in molecules and solids can be calculated in O(N) in at least three ways: i) using fast Fourier algorithms, ii) using a generalization of the Greengard algorithm [5,6] or iii) using a generalization of the Ewald method to overlapping continuous multipoles on each atomic site [7]. The latter method is currently used in Dmol^3 for solids and large molecules, in the smaller molecule regime the older O(N^2) method is faster. The small errors which arise from using an auxiliary basis for the electrostatics calculation can be kept under control either i) by making the static energy stationary [8] wich appears to lead to an O(N^3) method, but is efficient for small to medium molecules, or ii) use the Harris functional energy formula to let truncation errors of the auxiliary density only show up in second order [9,10,1] . The latter approach has been demonstrated to be useful as an O(N) algorithm. It should not be confused with the very useful Harris approximations, which rely on a spherical superposition density as the auxiliary density.

There have been many applications of this program, but most have not been published because of industrial confidentiality restrictions. Ref. [11] may help to give an impression.

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Condensed matter calculations with Gaussian basis sets

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We developed a new density functional theory program for periodic systems. Kohn-Sham orbitals are expanded in atomic response basis functions that are given as a linear combination of Gaussian functions. Basis set parameters are optimised in atomic ground state calculations [1]. The best basis sets result from calculations where the atoms are placed into a parabolic confinement potential to mimic the contraction due to the environment. We use newly developed Gaussian pseudo potentials [2,3] to integrate out core electrons. Due to their analytic form and their fully separable non-local part, all matrix elements of the pseudo potentials can be calculated as two- and three-centre analytic overlap integrals over Gaussian functions. Besides the reduction of the number of electrons that have to be treated explicitly, pseudo potentials allow the use of smaller numbers of Gaussians for the basis set expansion.

In the spirit of the projector augmented-wave (PAW) method [4] we decompose the electronic density into three parts

$$\rho(r) = \tilde{\rho}(r) + \sum_A \rho_A(r) - \sum_A \tilde{\rho}_A(r)$$

where $\tilde{\rho}$ is a smooth density and ρ_A and $\tilde{\rho}_A$ are non-spherical atomic densities calculated by projector methods from the full density $\rho(r)$ [5]. Once this decomposition is made we can use the PAW form for the exchange and correlation and Hartree energy [4]. The big advantage of this form is that terms involving the smooth density $\tilde{\rho}$ are no longer coupled to the one-centre densities ρ_A. All energy terms of ρ_A and $\tilde{\rho}_A$ can be efficiently calculated using analytic integration for the Hartree terms or atom-centred numerical grids for the XC-functionals. The smooth density $\tilde{\rho}$ is expanded into a plane wave basis. We have shown that this approximation can be easily controlled and that all resulting matrix elements can be calculated analytically [6]. To achieve near linear scaling in the build-up of the Kohn-Sham matrix it is necessary to calculate $\tilde{\rho}$ and the above-mentioned matrix elements approximately from their real space formulas. The accuracy of the matrix elements is controlled by the energy cutoff of the plane wave expansion and a threshold for the inclusion of real space points.

We have tested the accuracy of our approach by calculating a set of small molecules. The scaling performance of the code was verified with respect to system and basis set size. We find an effective sub-linear scaling with respect to the number of basis functions per atom and an N log(N) type scaling (N: system size) for the Kohn-Sham matrix build-up. Diagonalisation becomes dominant at about 1500 basis functions. We have started to investigate alternatives to diagonalisation and first results will be presented.

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Recent developments in order N density functional theory

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Density functional theory has had tremendous success in recent years, finding a place in the modelling of systems in physics, chemistry and materials science to name but a few. One drawback as it stands is that it scales with the square of the number of atoms in the system, and asymptotically as the cube of the number of atoms. This scaling is crippling, allowing only a two-fold increase in the number of atoms for a ten-fold increase in computing power. We describe a method intended for use on highly parallel machines which can achieve the accuracy of traditional methods such as plane waves and which has only two parameters for systematic improvement of the energy, yet which scales linearly with the number of atoms in the system[1-4].

By a simple mathematical transformation, density functional theory can be rewritten in terms of the density matrix, $\rho(\mathbf{r},\mathbf{r}') = \sum_i f_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')$. The energy can then be written as a function of ρ (for certain contributions as $2\mathrm{Tr}[\rho H_{\mathrm{contrib}}]$), and the electron number as $2\mathrm{Tr}[\rho]$. Rather than attempt a minimisation of a six-dimensional function, we write $\rho(\mathbf{r},\mathbf{r}') = \sum_{i\alpha,j\beta} \phi_{i\alpha}(\mathbf{r})\ K_{i\alpha,j\beta}\ \phi_{j\beta}(\mathbf{r}')$, where $\phi_{i\alpha}(\mathbf{r})$ are localised orbitals, centred on the atom i. To maintain idempotentcy, we use the McWeeny transform, $\rho = 3\sigma\cdot\sigma - 2\sigma\cdot\sigma\cdot\sigma$, with $\sigma(\mathbf{r},\mathbf{r}') = \sum_{i\alpha,j\beta} \phi_{i\alpha}(\mathbf{r}) L_{i\alpha,j\beta} \phi_{j\beta}(\mathbf{r}')$; K can now be written $K = 3LSL - 2LSLSL$, with S the overlap matrix: $\int \phi_{i\alpha}(\mathbf{r})\phi_{j\beta}(\mathbf{r})\mathrm{d}\mathbf{r}$. The matrix L has a cutoff imposed on it, $L_{ij} = 0, \mid R_i - R_j \mid > R_L$, which effectively localises ρ.

The localised orbitals $\{\phi_{i\alpha}\}$ are non-zero only within a *localisation region* of radius R_{reg} (N.B. $R_{\mathrm{reg}} \neq R_L$). These localised orbitals are represented by the sum of short-range 'blip' functions (B-splines) on a cubic grid ('blip grid') which moves with the atoms[4]. Integrations (e.g. $\int \mathrm{d}\mathbf{r}\phi_{i\alpha}(\mathbf{r})\phi_{j\beta}(\mathbf{r}) = S_{i\alpha j\beta}$) are performed on a real space grid. Self-consistency is achieved with Pulay mixing of Kerker preconditioned (i.e. $\rho'(\mathbf{k}) = \rho(\mathbf{k})k^2/(k^2 + k_0^2)$) charge densities.

It is important to understand what each processor on the machine will be responsible for. The tasks can be divided into clear areas: a certain portion of the real-space grid for integration; certain atoms, and all rows corresponding to those atoms; the blip-to-grid transforms for those atoms; the forces for those atoms; certain columns of data for FFTs.

The main loop of the program can be summarised as follows: For a given set of localised orbitals, an initial Hamiltonian and potential are generated; the energy is then minimised with respect to the elements of the density matrix, and the potential and Hamiltonian are adjusted, until a selfconsistent solution is achieved; the localised orbitals are then varied so as to decrease the energy of the system, and the density matrix loop is repeated for the new orbitals; the minimisation with respect to the localised orbitals is repeated until the ground state is achieved. Once the ground state is achieved, forces can be calculated [5] (which are in exact agreement with the gradient of the energy), atoms moved and the search for the ground state repeated.

A key test of any code is how well it performs in an actual implementation. As CONQUEST is designed to be run on highly parallel machines, the question of how well it scales with processor number, as well as the linearity of scaling with atom number, needs to be addressed. Results which show that both of these forms of scaling are excellent will be presented, for systems of up to 6000 atoms[3].

One of the difficulties encountered in searching for the electronic ground state in general is that of ill-conditioning: certain variations of the degrees of freedom which produce only a very small change in the total energy. In the framework of CONQUEST, we have identified three such forms[6-8]: Length scale (well-known from plane wave codes); superposition; and redundancy. The form of the latter two will be outlined, and a solution for length scale ill-conditioning will be presented[8].

CONQUEST is in an extremely good state: we have all the elements needed for a successful atomistic code in place (initialisation, ground-state search and exact forces), and have performed trial relaxations successfully. All that is needed is robustness and optimization to ensure efficient use of computer time. We will be tackling other forms of ill-conditioning mentioned above, and improving the localised orbital representation, among other areas.

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A Quantum Chemical view of surfaces:

establishing relations between chemical bonding and observable properties

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One important objective of calculations of the electronic structure of matter is to reliably and accurately compute the energetics and other properties of chemical interactions and reactions. Powerful quantum mechanical computational methods have been developed which allow the properties of extended systems, including solids, interfaces, and surfaces, to be determined through detailed atomistic simulations. Recent advances in these methods are well represented in the presentations being given at this CECAM workshop. A second, extremely important objective of electronic structure calculations is to relate the properties of extended systems to fundamental chemical and physical concepts and to identify the mechanisms which lead to observed properties, especially to the shifts of these properties between different but related systems. This second objective of theoretical studies provides the basis for a predictive and global understanding of measured quantities in terms of the basic atomistic properties of matter. This review will be concerned with demonstrating how one may determine the underlying mechanisms for properties arising from the interaction of adsorbates with solid surfaces; however, the mechanisms and processes which are identified are also important for other forms of condensed, extended systems. The surface electronic structure is described using local orbital methods to determine ab initio wavefunctions for clusters of atoms designed to model or simulate the adsorbate-substrate interaction. These clusters have a special value because they allow on to focus on local aspects of surface chemistry, especially of the chemisorption bonding [1].

This molecular orbital cluster approach is also valuable because powerful methods exist which make it possible to analyze the electronic wavefunctions and to identify the consequences of the chemical bonding for various properties. It has been most common to describe the character of chemical bonds through the use of Mulliken Population analyses [2] and closely related methods; these methods are used to ascribe effective atomic charges and hybridizations. However, there are many examples where population analyses give quite misleading indications of the nature of chemical bonds including (1) characterization of metal-carbonyl bonds in complexes [3] and at surfaces [4] and (2) descriptions of the extent of charge transfer in metal oxides [5]. Indeed, it appears that Mulliken was aware of the limitations of population analyses [6]. In order to analyze the cluster wavefunctions and to identify chemical mechanisms, three methods which avoid the uncertainties of a population analysis will be used. One method is the projection of atomic or molecular orbitals on the cluster wavefunctions to determine the involvement of these orbitals in the bonding [7]. A second involves examining dipole moment curves [7,8], especially as a way to estimate charge separation or effective charge transfer. The final set of methods involves using constrained variations to determine or measure the contributions of various aspects of the interaction to energies and to other properties. A detailed decomposition of these contributions is given with the constrained space orbital variation, CSOV, procedure [9,10]. A contribution of particular significance in the CSOV procedure is that obtained simply from the superposition of the fixed or frozen charge distributions of the adsorbate and the substrate. This superposition of the fixed, or frozen, charge distribution makes it possible to distinguish "physical" effects from those which arise due to "chemical" modifications of the charge density.

In this review, examples will considered which show how different properties of chemisorbed systems reflect and are related to the chemical bonding and other interactions of the adsorbate with the substrate. For each example, there are accepted relationships used to infer the significance of observed properties in terms of the character of the chemisorption bond. It will be shown that these accepted relationships are, in the examples considered, incomplete and that they neglect essential features of the way that the interaction affects the properties.

The first example concerns the penetration of adsorbates below the surface and into the bulk; adsorbates which penetrate the surface are likely to react with the substrate and form complexes and compounds. The penetration of F [11], a representative halogen, and of Na [12], a representative alkali metal, into a Si(111) surface is compared. In general, size is considered as a key property which determines whether an adsorbate is sufficiently small to penetrate a surface or whether it is too large and will remain above. Seel and Bagus [13] and Bagus [11] showed that the charge state of an adsorbate interacting with a semiconductor surface also has an important influence on the energetics of surface penetration. The electric fields arising because a charged adsorbate is present could draw the adsorbate toward and into the surface. Thus, F/Si(111) which adsorbs as F^- has minima both above and below the surface and there is no barrier to surface penetration. A similar penetration without a barrier might be expected for Na/Si(111) which adsorbs as Na^+ but this is not found [12]. For Na, there is only a shallow well below the surface and a barrier of $\sim$ 3 eV to surface penetration. The origin of the asymmetry between anionic and cationic adsorbates been identified by examining the idealized, perfect ionic limits of point charges of $Q = -1$ and $Q = +1$.

The other two examples reviewed concern: (1) The interpretation of the shifts of valence level ionization energies, or binding energies (BE's), of adsorbate levels between free and chemisorbed molecular systems. And, (2) the origin of the shifts of the intra-molecular vibrations of adsorbed molecules with respect to the energies of vibrations in the free molecule. The relative shifts of different adsorbate levels are commonly interpreted as indicating the involvement of an orbital in forming chemical bonds with the surface; thus, a shift to higher BE is often described as a bonding shift. A more careful analysis [14] shows that such shifts may actually indicate the adsorbate geometry rather than the bonding character. A major origin of shifts of molecular vibrations is commonly taken as arising from changes in the occupation of molecular orbitals of bonding and anti-bonding character when the chemisorption bond is formed. While this is indeed a contribution to the shifts of vibrational energies, a decomposition of the origin of these shifts shows that a surface wall effect, arising because of Pauli or steric repulsions of the adsorbate with the surface, must be considered [15].

The detailed analysis of wavefunctions for cluster models of surface interactions can be used to separate various physical and chemical terms which is normally difficult with experiments. An important goal of atomistic cluster model studies is to combine experimental and theoretical information to obtain broad, and unified, views of surface phenomena.

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Periodic *ab-initio* HF and DFT calculations with a Gaussian type local basis set for large unit cell systems.

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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 and Kohn-Sham 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 in the most recent version of the code.

The Coulomb infinite series are always evaluated analitically, 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, the exchange-correlation potential is expanded in an auxiliary basis set of Gaussian-type functions, with even tempered exponents. For the numerical integration, the atomic partition method proposed by Becke [5] has been adopted, combined with the Gauss-Legendre (radial) and Lebedev(angular) quadratures.

Recent improvements with respect to the public version of the code [6] permit to use a basis set of symmetry adapted crystalline orbitals (SACO's) 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 [6,7]. It is then possible, in these conditions, to numerically optimize the geometry of complex structures at a relatively low cost.

Three different examples have been discussed during the workshop:

1) All silicon faujasite (144 atoms in the unit cell; see figure 1); the geometry has been fully optimized at the HF level; its relative stability with respect α-Quartz [8] has been evaluated with different hamiltonians(see table 1).

2) F centers in LiF by using a supercell approach, and comparing the results of supercells containing 8, 16, 32, 64 and 128 atoms, both at the HF and LDA level.

3) The equilibrium structure of pyrope $Mg_3Al_2Si_3O_{12}$ (80 atoms/cell, see figure 2), and its stability with respect to simple oxides MgO, Al_2O_3 and SiO_2 as a fuction of pressure [9].

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Figure 1. Crystalline structure of silico–faujasite. Only silicon atoms are shown. (A): framework viewed along the [111] direction; (B): primitive cell and its elementary vectors. The four types of O-bridging atoms are also shown. (PostScript file available upon request; email to ordejon@condmat01.geol.uniovi.es)

Figure 2. Sketch of the garnet structure: $X_3Y_2Z_3O_{12}$; in pyrope, X=Mg, Y=Al and Z=Si; X and Y are at the center of the tetrahedra and octahedra, respectively; Mg is eight-fold coordinated, and is at the center of a triangular dodecahedra. (PostScript file available upon request; email to ordejon@condmat01.geol.uniovi.es)

Table I Dependence of the stability of faujasite with respect to α-Quartz as a function of the adopted hamiltonian: Hartree-Fock, *a posteriori* corrections (lines 2-4), density functional (lines 5-7), B3LYP hybrid (last line). The basis set is a 6-31G* and 6-21G* for oxygen and silicon, respectively; in all cases the same geometry has been adopted; in the third column the total energy (in Hartree) per SiO_2 unit is given; in the fourth column data are in kJ/mol.

		α–Q	FAU
HF		-438.883311	7.36
A posteriori	VWN	-441.113002	7.70
	LYP	-440.077555	11.51
	PW-GGA	-440.083692	7.74
Full DFT	S-VWN	-437.953720	13.79
	B-LYP	-440.106909	7.66
	PW-PW (GGA)	-440.073140	10.37
hybrid	B3-LYP	-440.037495	8.36

Direct determination of Wannier functions and their use for explicit calculations of the correlation energy

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Starting from fully localized guess orbitals it is possible to obtain directly occupied and virtual SCF orbitals, i.e. Wannier functions for a periodic system, without a preliminary obtention of the canonical (i.e. Bloch) orbitals and their subsequent transformation. The guess orbitals are of bonding or antibonding character, or of atomic character for core occupied orbitals or for

virtual oscillating orbitals. The procedure is iterative, it starts with a preliminary hierarchized orthogonalization of the guess orbitals, followed by a simplified Configuration Interaction of the reference determinant and the singly excited ones. The coefficients of the single excitations are used to to give the proper delocalization tails to the occupied and virtual orbitals, which are reorthogonalized, the process being repeated to the satisfaction of Brillouin's theorem. Due to possible cut-offs in the calculation of integrals, the process scales as the number of atoms for finite molecules and clusters. For periodic systems, taking benefit of the translational invariance, one only needs to obtain the orbitals centered on a given cell.

These orbitals may be used for an explicit calculation of the correlation energy per cell, coming from double excitations involving at least one hole in the reference cell. Their coefficients may be calculated to various degrees of accuracy, from MP2 to Coupled Cluster, taking benefit of the rapid spatial decrease of the orbitals.

Test calculations will be presented on 1–D model problems. They illustrate the efficiency of the method for for insulating systems, for which the 3rd and higher order contributions of the propagation of holes and particles converge rapidly. The hole-particle attraction is shown to play an important role and is easily taken into account.

For gap-less problems the method faces two difficulties. The first one is the symmetry breaking of the Hartre-Fock solutions; starting from these solutions the calculated correlation energies are severely underestimated. Even when using the Wannier functions which are transformed from the symmetry-adapted Bloch functions, and which have long-range delocalization tails, the explicit calculation of the correlation energy is difficult, due to the slow convergence of the series of diagrams propagating the holes and particles.

Hence the method seems a promising tool for insulating materials while progress is needed for the localized treatment of metals. Finally it is shown how one may easily calculate correlated band structures from the Wannier functions.

Direct determination of Wannier functions and local correlation-energy increments in solids

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The first part of the talk focuses on attempts to directly determine Wannier functions in polymers and solids, at the ab-initio Hartree-Fock (HF) level. In a recently published scheme [1], we treat the Coulomb interaction of a chosen local region with the surrounding solid by means of Ewald techniques, exchange is evaluated in direct space, and a Huzinaga-like shift operator is used as a localization device. When self-consistency is reached both with respect to the embedding and the localization potentials, we obtain excellent agreement with Bloch-orbital-based results of other groups. Applications so far have been done for ionic solids (alkali hydrides, halides, oxides) and t-PAC; properties considered are lattice constants, bulk moduli, cohesive energies, Compton profiles, band structures. Extension of our approach a) to allow for non-orthogonality of the localized orbitals, and b) to include electron correlation effects, by means of a local scheme (cf. below) is currently underway.

Possibilities for explicitly treating post-HF many-body effects, at a wave-function level, are reviewed in the second part of the talk. Application of quantum-chemical configuration-interaction like schemes requires localization both in the occupied and virtual spaces. Exploiting the local nature of the dynamical correlation hole, we use a cumulant expansion in terms of correlation contributions of increasingly larger sets of localized-orbital groups, within the occupied space. The increments so defined turn out to be rapidly convergent with respect to the distance and number of localization centres. They even turn out to be well transferable from finite clusters (ions embedded in a Madelung field of point chrges, or covalently bonded clusters with dangling bonds suitably saturated) to solids. This enabled us to determine electron-correlation effects on ground-state properties and valence-band structures of a variety of semiconductors [2], ionic crystals [3], and polymers [4], using quantum-chemical ab-initio methods; even d- and f-elements could be treated this way [5], at a coupled-cluster level with up to triple excitations. Basing the scheme on rigorously derived Wannier functions (cf. above) will extend its range of applicability, while introducing restrictions in the virtual space according to the local correlation scheme of Pulay and Werner [6] is expected to further enhance its efficiency.

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Strategies for "cheap" Configuration Interaction in molecules

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INTRODUCTION AND MOTIVATION

I will speak about our work combining the pseudospectral method with local correlation approximations to configuration interaction (CI). In the world of molecular quantum chemistry, there is still a significant group of people that believe that ab initio electron correlation methods that can be systematically improved are preferable to current implementations of density functional theory where such systematics is as yet not available. Of course, up to the present, the prohibitive scaling (with system size) of ab initio correlation methods such as perturbation theory, configuration interaction, and coupled cluster methods ($N^5 - N^8$), where N is the number of basis functions) has limited their applicability to large systems. By contrast, the attractive scaling of density functional theory (N^3 in its traditional formulation but as low as $N \ln N$ in current O(N) schemes) provides the ability to examine large systems, albeit with the caveat that one never knows how reliable the functionals are (since they are not known exactly). My goal has been to retain the systematics and accuracy characteristic of configuration interaction, while finding ways to reduce the scaling of the method so that large systems may be studied relatively inexpensively.

BACKGROUND

For those of you who may be unfamiliar with configuration interaction, it takes as an ansatz that the exact many electron wavefunction may be expressed as a linear expansion of N-particle determinants (typically spin-adapted to be eigenfunctions of S^2 in addition to S_z). These "electron configurations" are composed of some approximate ground state wavefunction (e.g., Hartree-Fock, HF, or a multiconfiguration selfconsistent field wavefunction such as Generalized Valence Bond, GVB, or Complete Active Space Self Consistent Field, CASSCF) and typically configurations that involve single and double excitations of electrons from occupied orbitals to unoccupied (virtual or external) orbitals in one of the configurations comprising the ground state. This type of technique is called SDCI (or CISD) when the excitations are from an HF wavefunction or MRSDCI if the excitations are from multiple reference (hence the MR) states, as in the case of GVB or CASSCF. The beauty of the CI technique is that one can systematically expand the N-particle basis (the number of spin-adapted configurations) until quantity of interest is converged. The principal disadvantage of this technique is its expense. (Another disadvantage often mentioned is the lack of size-consistency; in practice, once a multi-reference wavefunction is used for the ground state in the CI, the size-consistency error is extremely small.)

The expense of conventional SDCI has three aspects: operation count, fast memory usage, and disk storage. The overall operation count of the method is considerable, since it scales as N^6. Storage of the CI expansion coefficients (the so-called CI vector) in fast memory is critical, and this scales as $n^2 {N_v}^2$, where n is the number of occupied (or internal) orbitals and N_v is the number of virtual orbitals. Disk storage of the all-external two-electron integrals, which are often labelled $(ab|cd)$, increases as ${N_v}^4$. I will present work that addresses all three issues.

TECHNICAL APPROACH

We have been exploring the use of pseudospectral evaluation of the two-electron integrals in electron correlation (CI and perturbation theory) calculations for some time [1]. The pseudospectral method, which originated in the world of computational fluid dynamics [2], was brought into the quantum chemistry community by Friesner [3]. It is a dual grid/analytic basis function technique which replaces analytic two-electron integrals $(ab|cd)$ with a product of three terms. First, the so-called collocation matrix, R_{gb}, is constructed, which is simply the basis set evaluated at each grid point. The collocation matrix transforms the function from spectral (function) space to physical (grid) space and once in grid space, one evaluates the Coulomb operator on the grid. The Coulomb operator on the grid is simply the set of three-center one-electron integrals, $A_{cd}(g)$. Analytic evaluation of these ensures an accurate representation of the Coulomb operator and the evaluation is trivial when the functions are Gaussians. Finally, one must transform back to spectral space via the inverse transform, Q_{ag}. (There are many issues associated with the construction of Q that are not germane to the discussion here - note that generally R and Q are not square and therefore the inverse is not uniquely defined.) Thus, $(ab|cd)$ is approximated as a sum over grid points of the quantities $Q_{ag}A_{cd}(g)R_{gb}$, where $abcd$ are basis function indices and g is a grid index. Why do this? The algorithm can be constructed so as to scale as MN^2, where M is the number of grid points, and since $M \approx 10N$, one can see that a scaling advantage of N can be achieved. In practice, we have found as much as an order of magnitude speedup for perturbation theory calculations.

While this addresses reduction of operation count and storage of the two electron integrals, the bottleneck that remained in our pseudospectral correlation methods was the storage of the CI vector in fast memory. This quickly gets out of hand for even moderately-sized molecules because of the $n^2 N_v^2$ scaling. Thus, we began our local correlation work, which exploited the pioneering work of Saebo and Pulay [4], who applied their ideas to conventional spectral calculations. Saebo and Pulay approached the idea of local correlation in two ways. One was to localize the occupied space and then to make use of the fact that simultaneous correlations of electrons that reside far away from one another should be small, in order to eliminate configurations from the CI vector and hence reduce the memory requirement. This was referred to as the "weak pairs" approximation. More importantly, however, was the idea that the remaining electronic excitations should be adequately described within a truncated virtual space. By this I mean that the functions needed to represent the external space in the CI for a given pair of electrons being excited should be resident near the location of those two electrons. That said, the strategy was to abandon the concept that one needed to excite electrons to all virtuals but rather to create domains for each pair of electrons consisting of the union of the atom-centered basis sets resident in the region of these electrons. (Again, there are non-germane technical issues associated with, e.g., eliminating linear dependencies, etc.) By limiting the domain of virtuals accessible for each electron, one again limits the size of the CI vector. This last approximation has been referred to as the "truncation of the virtuals" approximation. The beauty of this latter approximation is that because the average domain size will not grow with the size of the system, it effectively becomes a prefactor in front of an n^2 scaling for large systems. This work was not only appreciated by us, but also by Friesner and coworkers [5] and by Hampl and Werner [6], who applied Pulay and Saebo's local correlation technique to second order perturbation theory and coupled-cluster methods, respectively. In this latter work, as in the work of Pulay and Saebo, the treatment of the all-external two-electron integrals became the bottleneck since the size of the CI vector was no longer an issue. We have shown how this bottleneck can be eliminated by employing pseudospectral methods to evaluate the all-external two-electron integrals in the full AO basis [7bc].

RESULTS AND IMPACT

What we have done in the last two years is to combine pseudospectral methods that address operation count and storage of the two-electron integrals with both types of local correlation - localization of the internal space and localization of the external space - which address the memory needs by reducing the size of the CI vector [7]. I will discuss the effect of: (i) localization of the internal space combined with pseudospectral techniques, (ii) localization of the external space combined with pseudospectral methods, and (iii) simultaneous implementation of both local correlation schemes with pseudospectral methods. We find that accuracy can be maintained while simultaneously achieving significant speedups and dramatic reductions in disk storage requirements even in modestly-sized molecules.

FUTURE WORK

We have implemented this thus far only in the relatively useless method of SDCI. Our next task is to implement this within the far more useful and accurate method of MRSDCI, and then to parallelize the algorithm, as we have done in the past with pseudospectral MRSDCI [8]. At that point, we hope the algorithm will be useful for many applications on relatively large systems.

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Linear-scaling Density-Functional with atomic orbitals

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For electronic-structure calculations, the scaling of computational load with system size has become of great importance in the last few years. Traditional approaches require an order of magnitud progress in computer power, just to double the size of the largest system that can be studied. The last five years have witnessed very active research in linear-scaling algorithms for the purpose. They were very succesful from the start for empirical or semiempirical Hamiltonians, and opened the door to larger and more complex systems. However, further progress was needed to obtain linear scaling on an otherwise standard ab-initio scheme: within a self-consistent one-particle approach, a linear-scaling substitution of the diagonalization problem is not enough, since obtaining the Hamiltonian must be linear-scaling as well. This is the main point of this session.

It is clear that a linear-scaling approach will be eventually more favorable than a traditional higher-scaling one. It has been found, however, that the question on *when* this happens is still important, especially when the turn-over size for a specific kind of approach is still very large.

This has turned out to be the case in approaches using systematic basis sets (like plane waves). The higher efficiency of LCAO permits, however, to take advantage of linear-scaling algorithms right now.

The key idea in linear-scaling algorithmics is localization. Imperative to achieve linear scaling is a description based on localized entities. For instance, the diagonalization problem can be addressed by looking for localized (Wannier) functions instead of extended (Bloch) ones. Similarly, building of a selfconsistet Hamiltonian can be achieved more naturally when using a localized basis for its representation. Again, LCAO presents itself as especially suited for the purpose.

The computation of all the selfconsistent Hamiltonian terms within a LCAO scheme is complicated and expensive. At the level of density-functional theory (normally more efficient than other first-principles approaches) it requires the calculation of four-center integrals for the Hartree term, which cannot be done straightforwardly in an efficient way. Non self-consistent approaches (Harris functional) go around the problem since the off-diagonal terms in the density matrix are zero, and no four-center integrals are thus needed, but the inability to obtain selfconsistency represents an important limitation in general.

A linear-scaling fully self-consistent DFT methodology was obtained three years ago [1,2]. The key to the linear-scaling self-consistent Hamiltonian was the idea of calculating the problematic terms of the Kohn-Sham Hamiltionian by integrating on a real-space grid. Other terms (including the kinetic-energy matrix) were calculated within LCAO philosophy. This mixed approach plus the extensive use of sparse-matrix techniques, proved to be very efficient. The Coulomb problem, traditionally a hard one within LCAO, is trivially solved with well-established numerical algorithms. The real-space grid technique has been later used by other authors [3,4]. In our group, the further development and generalization of this mixed technique has led to the SIESTA program [5], a linear-scaling general-purpose DFT program especially thought for first-principles calculations of large systems.

As a consequence of the use of a real-space grid, smoother wave functions and densities represent less computational effort. Core electrons are thus replaced by smooth pseudopotentials, for which there is a large body of experience within the solid-state community. SIESTA uses several pseudopotential schemes [6,7] in the factorized form proposed by Kleinman-Bylander [8].

The SIESTA program can use any LCAO basis, since, unlike most traditional LCAO first-principles schemes, it deals with the radial part of the basis functions numerically. The two-center LCAO matrix elements are calculated numerically at the beginning of any simulation and stored in tables for subsequent use. Three- and four-center integrals are dealt with in the real-space grid. The program is, therefore, not bound to Gaussian functions nor to any other shape. This flexibility is very useful for adaptating of the basis functions to the specific forms of pseudopotentials at the core region, but also to describe adequately the decay towards vacuum at a surface, for instance.

An additional important consideration about the atomic orbitals is their finite range. Within this scheme, linear scaling is obtained when explicit use is made of localization. It can be done in two ways: either neglecting matrix elements between distant orbitals (by whatever criterion), or using basis orbitals that strictly vanish beyond a cutoff radius [9]. We have adopted the latter. The main advantage is consistency: given a basis, the problem is solved exactly. It is numerically very stable even for short ranges (while the first approach is very delicate when using small ranges with non-orthogonal bases [10]). The basis range represents in any case an additional approximation which should be controlled by converging the relevant results versus range. The computational load grows substantially with the basis range, and it is therfore important to work with basis functions that display fast convergence for short basis ranges.

Even though SIESTA admits any user-provided basis, we have been mainly working with ideas of the finite-range pseudoatomic orbitals proposed by Sankey and Niklewski [9]. They are the result of solving the DFT atomic problem (pseudopotential included) with the boundary condition for the orbitals of being zero beyond a given radius. For an equivalent degree of convergence, the cutoff radius depends on the species, and also on the specific orbitals. We have proposed a systematic way of finding the different cutoff radii as a function of a single parameter that defines the finite-range approximation: the energy shift. All pseudoatomic orbitals shift upwards in energy when confined to a sphere; defining this energy shift gives all the required radii, guaranteeing a balanced basis.

Other ways of defining finite-range orbitals have been proposed [4] and there is definitely field for improvement in this aspect, including algorithms for smoothly cutting longer-range orbitals (which should ensure fast convergence with cutoff radius while offering a way of procuring balanced bases).

The mentioned desired features of atomic bases makes them different from the ones developed over the years in the quantum chemistry community. It would be a waste, however, if the accumulated knowledge would not be used, especially considering the fact that atomic bases are not systematic, and that scientific input is needed to be sure of having bases of the desired quality. We thus incorporate old ideas into new schemes adapted to numerical bases for linear scaling.

Numerical multiple-ζ bases are constructed in the split-valence philosophy. Given an atomic orbital, it is split into two or more functions. The first splitting is made by introducing a smooth function that reproduces exactly the tail of the original orbital beyong a specified radius. The difference between the original orbital and this smooth function is an orbital with an even shorter range. Multiple splits are obtained by repeating the procedure.

SIESTA also allows for polarization orbitals. They are obtained by numerically solving the problem of the isolated atom in the presence of a polarizing electric field. Comparing the solution with a perturbative expansion gives the shape of the wanted polarization orbitals. Also diffuse functions, off-site orbitals and remaining artillery can be used within SIESTA. Basis set superposition errors can be computed as well.

The described ideas put together give a flexible tool for the study of quite varied problems. It has already been applied in the last two years to different systems, ranging from tests on simple solids and small molecules, to a double-helix of DNA in its dry A configuration. Metallic clusters of Au and of Ni, large carbon fullerenes, carbon nanotubes, fullerenes and nanotubes on Si and Au surfaces, are systems for which interesting results have already been obtained, and which give an idea of the applicability and flexibility of the approach. We have worked with systems of close to one thousand atoms in realistic studies, and up to 4000 Si atoms when testing the performance. All these calculations have been performed on scalar workstations.

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Occupied subspace invariant variational Kohn-Sham DFT through third derivatives

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The rapid pace of advances in computational power and the advent of parallel processing demands comparable advances in algorithmic development. Computational materials science now holds the promise of accurate and realistic calculations of experimental measurables on complex materials. However, with tried and true traditional algorithms, accurate quantum mechanical calculations of materials properties are typically limited to system sizes of less than a couple hundred atoms. This is due to the unphysical, fast scaling with size, typically N^3 or greater. Linear response (or second derivatives) and related adiabatic time-dependent density functional theory often provides the connection to experimental measurements; but typically scale as N^3 (for absorption) or N^4 (for phonons). This presentation will discuss some advances towards generalizing linear scaling ground state calculations to linear scaling-linear response variational second and non-variational third derivatives. Adiabatic time-dependent density functional theory follow immediately from the linear response. The focus in this presentation will be more conceptual than algorithmic.

We will discuss several related concepts with regards to linear scaling. One common theme throughout the presentation will be the variational principle as a unifying concept and a derivational tool. We will show how all orbital-based and density-matrix based linear scaling methods follow from one consolidating variational principle. This then leads to a new way to look at uniqueness and at the gradient vector for iterative minimization. We will show that for non-orthogonal localized representations (such as LCAO or non-orthogonal tight-binding) few if any algorithms use the true energy gradient. Another major point will be a focus on invariance with respect to representation of the occupied subspace. In deriving an occupied-subspace invariant linear response algorithm we find that the response function can rigorously be related to the ground-state with a perturbing external potential and an unperturbed electron-hole Green's function. The electron-hole Green's function is dependent only on ground state variables. One can think of the spectrum of the derived electron-hole Hamiltonian as the virtual excitation space that the ground-state couples to under the action of an external perturbation. One then also gets a standard Fermi's Golden rule for time-dependent perturbation theory where the perturbing potential is the variation of the real external potential not the variation of the effective Kohn-Sham potential. Besides leading to an occupied-subspace invariant variational linear response algorithm that is order N for localized perturbations, it also leads to a potential connection to probes of the excited states. Finally we will show that variational second derivatives are numerically superior (as should be expected) to non-variational ones and that having variational second derivatives makes deriving and calculating third-derivatives relatively easy.

We will show phonon spectra obtained with this new algorithm for a vacancy in Silicon and for novel strained carbon structures. Time permitting we will show results of alchemical perturbation theory through third derivatives for Si-Ge

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Linear scaling electronic structure methods with Gaussian orbitals

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This talk will address our recent efforts in developing fast, linear scaling electronic structure methods for large scale applications. Of special importance is our fast multipole method (FMM) [1] for achieving linear scaling for the quantum Coulomb problem (GvFMM), the traditional bottleneck in quantum chemistry calculations based on Gaussian orbitals. Fast quadratures [2] combined with methods that avoid the Hamiltonian diagonalization [3] have resulted in density functional theory (DFT) programs that can be applied to systems containing many hundreds of atoms and –depending on computational resources or level of theory- to many thousands of atoms [4]. Three solutions for the diagonalization bottleneck will be analyzed and compared: a conjugate gradient density matrix search (CG-DMS), a Chebyshev polynomial expansion of the density matrix in terms of the Hamiltonian (CEM), and a pseudo-diagonalization method. Besides DFT, our near-field exchange method [5] for linear scaling Hartree-Fock calculations will be discussed. Based on these improved capabilities, we have also developed programs to obtain vibrational frequencies (via analytic energy second derivatives) and excitation energies (through time-dependent DFT) of large molecules like porphyn and C_{70}. Our GvFMM has been extended to periodic systems [6] and progress towards a Gaussian-based DFT and HF program for polymers and solids will be reported. Last, we will discuss our progress on a Laplace-transformed second-order pertubation theory (MP2) method for achieving better scaling with this method.

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Optimally localized Wannier functions

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The electronic structure of materials is often studied from first principles in terms of extended Bloch orbitals in periodic boundary conditions. It is well known that these Bloch orbitals can be transformed, in principle, into generalized Wannier functions (GWFs), i.e., orthonormal localized functions spanning the same subspace as is spanned by the given Bloch bands [1].

An understanding of these GWFs is of increasing importance for several reasons. First, the modern theory of electric polarization can be framed in terms of the displacements of the centers of charge of the Wannier functions [2]. Second, several very promising linear-scaling methods are already based on solving directly for a set of GWFs [3]. Third, the GWFs might play a role in the development of new linear-scaling or embedding schemes, or form an appropriate basis for treatments of electronic correlations, magnetic interactions, and the like.

However, the transformation from Bloch functions to GWFs is highly non-unique. Even for the single-band case, this non-uniqueness shows up as a phase freedom at each k-point. In the multiband case, there is more generally a free unitary matrix at each k-point. The non-uniqueness of the GWFs means that one cannot compute and display "*the* Wannier functions" in the way that one can for "*the* Bloch functions," and this may have contributed to an impression that the Wannier functions are ill-defined and therefore uninteresting.

We discuss here a method for resolving this non-uniqueness by determining the *optimally-localized* set of generalized Wannier functions for a given system [4]. These are closely analogous to certain "localized molecular orbitals" that have been discussed in the chemistry literature [5]. Although we minimize a functional that represents the total spread $\sum_n \left[\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2 \right]$ of the Wannier functions n in real space, our method proceeds directly from the Bloch functions as represented on a mesh of k-points, and carries out the minimization in a space of unitary matrices $U_{mn}(\mathbf{k})$ describing the rotations among the Bloch bands at each k-point. The method is thus suitable for use in connection with conventional electronic-structure codes.

The method is of interest for several reasons. (1) The optimally localized GWFs can often give interesting physical and chemical insight into the bonding in different classes of insulating materials. This will be illustrated especially for the case of molecules with double bonds, and for a-Si. (2) Such insight may ultimately help determine the choice of most efficient linear-scaling approach for a given class of materials. (3) The Wannier centers map the polarization field of the electronic ground state onto a discrete set of localized point charges, providing a classical description of quantum dielectric properties. For example, the Born effective charges Z^* can be decomposed not just band-by-band, but even GWF-by-GWF, giving additional insight into the spatial and chemical nature of the dynamical contributions to Z^*. (4) The formal structure of the theory is appealing, and several unanswered questions of a mathematical nature are raised by the work.

Applications to several molecules, semiconductors, ionic insulators, and perovskite ferroelectrics have been carried out to date. Several of these applications will be discussed [4, 6-7].

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Real Space Grids and Augmented Grids: a new look at mixed basis set methods.

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Plane-wave pseudopotential methods, such as Car-Parinello methods, are successful for several reasons. Firstly the FFT makes it simple to evaluate the real space wave function $\psi(r)$ at a grid of points, r, given the plane wave amplitudes, $c(k)$. Secondly the basis is complete. In principle it is straightforward to ensure convergence simply by changing a single parameter, the plane wave cut-off k_{max}. Thirdly the basis is unbiassed, implying that energy *differences* between different atomic configurations will have no systematic basis set superposition errors, and also that the Hellman-Feynman forces can be evaluated without Pulay correction terms.

Recently a number of groups have developed electronic structure methods based on real space grids. The methods inlcude finite differences, finite elements, b-splines, and wavelets. The grid methods retain many advantages of the plane wave codes, such as completeness and absence of basis set superposition errors. They also have the advantages of working entirely in real-space, and hence allowing the application of order N algorithms and of enhancing opportunities for parallel computing.

In many physical and chemical problems the unit cell contains atoms with very different characteristic plane wave cut offs, k_{max}. For example one might want to study a single transition metal impurity in a semiconductor. This is difficult for plane wave codes, since the real space grid, r, mus be uniformly spaced throughout the whole unit cell. Grid methods can do better in such systems since the grid density can be spatially varying. For exmaple the curved-space method does this very elegantly. Finite elements, as used in many engineering applications, are also very suited to varying grid densities. Wavelets allow a heirachy of grids of increasing density, and so again it is possible to evaluate $\psi(r)$ in one region of the unit cell with a much greater resolutions than in other regions. Wavelets are used in image-compression for exactly this reason.

On the other hand atomic orbital basis sets, such a Gaussians, also have many advantages. Calculations can be carried out in real-space, allowing efficient parallelism and use of O(N) algorithms. It is also no problem to use more basis functions for 'difficult' atoms. In most cases it is possible to use many fewer basis functions per atom than with plane wave or grid methods. On the other hand it may be difficult to estimate basis set superposition errors or to choose an optimised basis set which is equally accurate in different bonding situations (e.g. say sp^2 and sp^3 Carbon).

In this talk I shall discuss possible methods which combine the real-space grid methods with atomic orbitals. For example one can consider the analogue of the old Augmented Plane-Wave (APW) method, in which a real space grid is supplements by a set of suitable local orbitals. Such combined methods may offer the possibility of achieving small basis set sizes, comparable to the atomic orbital methods, and at the same time offering simple tests for convergence and completeness by increasing the grid spacing. I shall discuss possible ways that such mixed basis set methods may be implemented, and will illustrate possible advantages and disadvantages over either a purely atomic basis set, or a pure grid basis set.

Localized Spherical Wave basis sets

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Plane waves have proved to be a popular basis for *ab initio* calculations within the pseudopotential approximation as a result of their efficiency and simplicity. In particular, the construction of a plane wave basis set is a systematic procedure. Plane waves are the solutions of the free particle Schrödinger (or Helmholtz) equation subject to Born-von Karman boundary conditions, and the completeness of the basis is determined by a single parameter, the kinetic energy cut-off.

Solving the same equation subject to “hard sphere” boundary conditions appropriate to localized orbitals results in a set of truncated spherical waves. Within a single sphere, this set is orthogonal and its completeness can once again be controlled by a kinetic energy cut-off. As for plane waves, the spherical waves should prove particularly efficient when used with pseudopotentials.

The oscillatory nature of the spherical waves means that they are not naturally suited to numerical work. However, analytic expressions [1] for several key quantities needed during *ab initio* calculations can be derived by considering the Fourier transforms of the basis functions. These quantities are the overlap and kinetic energy matrix elements for basis functions confined within different spheres. Exploiting the separable form of the pseudopotential and expanding the non-local projectors in terms of spherical waves also allows the non-local pseudopotential matrix elements to be calculated using the results for the overlap matrix elements.

These analytic results have been implemented computationally within a new scheme to perform linear-scaling total energy calculations within density-functional theory. This scheme is based upon the use of the single-particle density-matrix as the central quantity [2,3] which completely describes the Kohn-Sham system of fictitious non-interacting particles within DFT.

The major obstacle standing in the way of efficient density-matrix methods is the non-linear idempotency constraint which must be obeyed by the ground-state density-matrix. Methods investigated so far include the use of a “purifying transformation” [2,4,5] to implicitly impose the constraint and the use of a penalty functional [6] to obtain a variational principle which results in an idempotent density-matrix at the minimum. However, the non-analytic behaviour of such a penalty functional at the ground-state minimum prevents the use of efficient minimization techniques such as the conjugate-gradients method.

The scheme to be presented involves the use of an analytic penalty functional to weakly impose the idempotency constraint. The resulting estimate of the ground-state density-matrix is therefore only approximately idempotent, with an error in the occupation numbers which decreases as the strength of the penalty functional is increased. The total energy calculated from this density-matrix is accordingly in error, due to the over-occupation of low-energy bands and under-occupation of high-energy bands. From the form of the penalty functional chosen, an analytic correction to the total energy can be derived which allows accurate estimates of the ground-state energy to be made from non-idempotent density-matrices.

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Efficient techniques for the computation of electronic structure of layered materials

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A Green's function technique is presented for the calculation of the electronic structure in layered materials, *i.e.* ones which are periodic in two dimensions but not the third. It builds on a well established layered Green's function approach, the computational effort of which, for a short-ranged basis, scales as $O(N_\perp N_{||}^3)$. Here $N_\perp$ is the number of orbitals normal to the periodic dimensions, and $N_{||}$ the number in the plane. In layers for which the potential is repeating, it is shown that the relevant Green's functions can be obtained in $O(1 \times N_{||}^3)$ steps from the eigenvalues and eigenvectors of the complex band structure. When there is an additional perturbation, the exact solution provides a basis for the approximate solution that is much more efficient than the standard $O(N)$ approach. For an adiabatically varying potential, a WKB-like approximation results, which can be systematically improved to whatever accuracy is needed.

Energy renormalization group method for electronic structure of large systems

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Given an effective Hamiltonian (for example in a tight binding (TB) model), the primary computational task in electronic structure is to calculate the corresponding density matrix (DM). For large systems, a desirable property is that the computational load increases only linearly with system size, the "linear scaling" property. Various linear scaling approaches were indeed proposed recently (review in ref. [1]). The methods are not limited to TB models, and are equally useful in self consistent field (SCF) forms of DFT where they must to be supplemented by linear scaling Hamiltonian-buildup techniques [2-4] .

There is however a basic limitation in the linear scaling methods, because they all exploit the "near sightedness principle"[5] or the exponential decay of DM correlations in real space [6-10] ("DM sparsity"). There are many highly interesting systems usually metals, where the DM is not sparse: two point correlations decay algebraically [8,9]. Even for semiconductors, where the band gap is small, the DM has long range correlation lengths so only for very large systems does DM sparsity show up. Linear scaling for these systems, although possible in principle, is hardly achievable in practice. In this talk we contribute to the effort of overcoming these limitations: we attempt to enhance the capability and scope of linear scaling to the difficult cases of non sparse DMs.

The DM can be considered as the zero temperature limit of the Fermi Dirac density matrix (FD-DM). The finite, high temperature FD-DM has correlation lengths approximately proportional to a power (typically between 0.5 and 1) of the inverse temperature [6-9]. Thus FD-DM correlation range is controlled by selecting a large enough finite temperature. If the HOMO-LUMO gap is large, the FD-DM approximates the DM excellently even at high temperatures. However, when the gap is very small, the temperature of the FD-DM must be respectively reduced and its range becomes large. Based on this picture, an alternative more useful approach to this "low temperature limit" of the DM is developed. The DM is related to the following telescopic sum of terms:

$$\rho = F_{\beta_0} + (F_{\beta_1} - F_{\beta_0}) + (F_{\beta_2} - F_{\beta_1}) + \dots$$

Each term focuses on an increasingly smaller energy interval around the Fermi level. Each term is sparse if described in a space spanned by coarse grained basis functions. A prescription to create these coarse grained spaces and sparse matrices is given.

The method is based on a renormalization-group (RG) point of view, where DM correlations are observed in varying length and energy scales [11]. We demonstrate that in a metallic band the range of the DM is an invariant of the RG transformation, a property attributed by RG theory to infinite correlation lengths [11]. The numerical RG approach presented here, called the energy renormalization group (ERG), is different from conventional real-space RG in which a super block is constructed from a given number of blocks in real space [12]. In ERG, it is the energy which is rescaled by a constant factor at each step. We use Chebyshev expansion methods [13] both for calculating the Fermi-Dirac (FD) matrix [14] and also for performing a renormalization step. This last step is inspired by filter-diagonalization [15].

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Structural and electronic properties of high temperature fluid selenium

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Fluid selenium is reported to undergo a semiconductor to metal transition at high temperature and high pressure. A considerable effort has been devoted to the experimental study of this transition, either by X-Ray scattering or by EXAFS measurements, but no fully satisfactory theoretical explanation has been proposed up to now to account for the unexpected behavior of this element. In particular, the observed decrease of the first shell coordination number with increasing temperature has not been explained. We present recent semi empirical (tight binding Monte Carlo) computer simulation results. The tight binding model relies on a set of electronic structure parameters that have been adjusted on ab-initio calculations. Our results shed a

new light on the processes involved when fluid selenium is submitted to extreme conditions of temperature and pressure. We show in particular that the metallic character of the liquid is related to the distribution of 1-, 2- and 3- coordinated atoms.

Tight-Binding calculation of the elastic properties of single-wall nanotubes

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We report theoretical predictions of the energetic, structural and elastic properties of single wall nanotubes. We shall discuss estimations of the Poisson ratio and Young modulus for C, BN, BC_3 and BC_2N nanotubes. We have focused attention on both arm-chair (n,n) and zig-zag (n,0) nanotubes, with n in the range 5 to 20. For the particular case of C nanotubes we have also considered a number of chiral examples. A brief outline of the theoretical methods will be given, followed by a discussion of the results obtained, paying particular attention to the elastic properties.

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Structure, energetics, and dynamics of Si adatoms on Si(100):

An O(N) Non-Orthogonal Tight-Binding molecular dynamics study

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Solid State Division, Oak Ridge National Lab
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STM studies of Si/Si(100) and Ge/Si(100) reveal chain structures at low coverages and low temperatures which are believed to play a key role in the initial stage of epitaxial growth [1,2]. The chain structures are composed of two-adatom units which are found to behave differently from other ad-dimers observed on Si(100). For example, the "adatom pairs" of the chain structure appear dark in the filled-state image and bright in the empty-state image, while the usual ad-dimers on Si(100) appear bright in both cases. Using an O(N) non-orthogonal tight-binding molecular dynamics study [3], we provide the direct evidence for the formation of metastable chain structures and the explanation for the nature of the anomalous ad-atom pairs on the chain structure.

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6 General Workshop/Conference Announcements

6.1 Trieste Workshop

"Ninth International Workshop on Computational Materials Science: Electronic Structure Theory and Simulations"

January 14-16, 1999

The bi-annual Trieste workshop, formerly denominated "TOTAL ENERGY", will take place on January 14-16 1999, in Trieste-Miramare.

Deadline for registration and housing request is November 15, 1998.
Deadline for poster abstract submission is December 1, 1998.

Further information, including registration form, is available at the URL:

http://www.ictp.trieste.it/ictp/smr.html under the heading smr1154.

The organizing committee

(S.G. Louie, M. Methfessel, and R. Resta)

6.2 CCP1 Study Weekend

Collaborative Computational Project (CCP) 1

Study Weekend

Ab Initio Molecular Dynamics

30 October - 1 November 1998

at CLRC Daresbury Laboratory
Warrington, WA4 4AD, UK

Important: Please note that there are still about ten places left if anyone would like to register.

Scope

The basic principle of ab initio Molecular Dynamics is the use of dynamics with an "on the fly" evaluation of the gradient. In addition, this method is often coupled with the propagation of the wavefunction using quasi-Newtonian or Schroedinger equations of motion. The Car-Parinello method is beginning to be used in quantum chemistry applications and is most commonly applied in the context of DFT with plane waves.

To a quantum chemist, ab initio Molecular Dynamics looks much like simultaneous wavefunction and geometry optimisation which can be efficient for large molecules. However, simulation of dynamics often gives new insights and is crucial for extended condensed systems such as liquids. Even though quantum chemistry techniques are capable of treating systems with increasing numbers of atoms, the application of dynamics methods in quantum chemistry is still in its infancy.

This study weekend brings together the established practitioners in the field from the Car Parinello community, as well with those who are beginning to use such methods in traditional quantum chemistry.

Programme

All speakers are requested to allow at least 15 minutes for discussion.

Friday, 30 October

Arrival: Accomodation at Daresbury Park Hotel and the Daresbury hostel

Saturday 31 Oct, am, Chairman Ian Hillier (Manchester)

08:30	Registration at Daresbury Laboratory
09:00-09.05	M. A. Robb (King's College, London) Opening Remarks
09:05-10.05	M. Parrinello (Max-Planck-Institut Stuttgart) Title to be announced
10:05-10:30	Coffee + Posters
10:30-11:30	Paul Madden (Oxford) Orbital-free density functionals in the AIMD simulation of metals
11:30-12:30	Michiel Sprik (Cambridge) Ab Initio Molecular Dynamics of Liquids and Solutions
12:45	Lunch (Daresbury Laboratory)

Saturday 31 Oct, pm, Chairman Nicholas Handy (Cambridge)

14:00-15:00	Berny Schlegel (Detroit) Ab initio classical trajectories on Born-Oppenheimer surfaces. Some aspects of hessian based integrators.
15:00-16:00	Todd Martinez (Illinois) Ab Initio Molecular Dynamics with Quantum Effects.
16:00-16:30	Tea + Posters Chairman Brian Sutcliffe (York)
16:30-17:30	Richard Bryce (Manchester) Cooperative Effects in Fluoride/Water Clusters
19:00	Bar and Dinner will be at the Daresbury Park hotel

Sunday 1 Nov, am, Chairman M.A. Robb (King's College, London)

09:00-10.00	Thanh Truong (Utah) Quantum Modeling of Reactions at Solid-Gas and Solid-Liquid Interfaces
10:00-10:30	Coffee + Posters
10:30-11:30	Andrew Willetts (Cambridge) Direct Energy Minimisation
11:30-12:30	Mike Payne (Cambridge) Finite Temperature Simulations of Zeolites and Metallic Surfaces.
12:30	Buffet Lunch at Daresbury Laboratory, departure.

Registration and Practical Details

Two accomodation options are available, the prices include 2 nights accomodation, meals and transport between accomodation and the meeting, which will be held in the Merrison Lecture theatre at Daresbury Laboratory.

1) The Daresbury Park Hotel: Cost 205 pounds

We have agreed a special rate for executive-class rooms at this local 4-star local hotel.

2) The Daresbury Laboratory Hostel: Cost 85 pounds

The Daresbury Hostel provides budget accomodation for users of the Synchrotron Radiation Source. The rooms are single occupancy with shared bathroom facilities.

3) No Accomodation option: Cost 40 pounds

A copy of this information, together with links to travel information and the registration form can be found on the CCP1 web page at

http://www.dci.clrc.ac.uk/Activity/CCP1

In the event of any problems with this page, (there have been some teething troubles associated with recent changes to server) the study weekend information is also available at http://www.dl.ac.uk/TCSC/QuantumChem/ccp1sw.html.

Please register using the on-line form, and send a cheque made payable to CLRC Daresbury Laboratory, to:

Mrs Shirley Miller,
CLRC Daresbury Lab,
Warrington WA4 4AD,
UK.

Poster presentations are welcome, contributors should send an abstract, (less than 1 page in length) with the remittance.

A limited number of hotel and hostel rooms have been booked, and these will be assigned on a first-come, first-served basis. Early registration is advised, after 30th September availability of rooms and the rates given here cannot be guaranteed.

Attendees should arrange to arrive directly at their accomodation on Friday evening, and can pick up copies of the programme for the meeting outside the Lecture Theatre on Saturday Morning.

Further queries may be directed to:

p.sherwood@dl.ac.uk or s.miller@dl.ac.uk (local organisation)
mike.robb@kcl.ac.uk and r.hall@man.ac.uk (scientific programme).

7 General Job Announcements

Micro-magnetic simulations

Graduate Student Position

INESC Lisbon

The solid state technology group at INESC and IST in Lisbon is looking for a Ph.D. student of non-portuguese citizenship to work in the simulation of micro-magnetic devices. The group has a strong experimental activity fabricating and testing thin-film magnetic devices, including spin-valve reading heads (led by Prof. Paulo Freitas), and experience in simulation of materials (led by Prof. José Luís Martins). The micro-magnetic simulations project combines fundamental research in the magnetism of thin films with the applied research of making better magnetic devices.

For an overlook of the solid state technology group, INESC and IST (the top engineering school in Portugal) see

`http://bohr.inesc.pt`,

the web page of José Luís Martins is

`http://bohr.inesc.pt/~jlm`,

the last preprint of our micro-magnetic simulations can be found at

`http://bohr.inesc.pt/~jlm/preprints`.

For more information please contact Prof. José Luís Martins at `Jose.L.Martins@inesc.pt` or INESC, Rua Alves Redol 9, Apartado 13069, 1000 Lisboa codex, Portugal.

8 Abstracts

Magnetic properties of Ni-Mo single crystal alloys: theory and experiment

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Abstract

The magnetization of $Ni_{1-x}Mo_x$ single crystals with x=4,6,8 and 10 % by weight have been measured at 4.2K using a vibrating sample magnetometer and a Superconducting Quantum Interference Device (SQUID). The magnetization of the alloy at these low concentrations and at 0 K have been theoretically determined by using the tight-binding linearized muffin-tin orbital method coupled with augmented space recursion. The theoretical data are compared with the experiment.

(Submitted to Journal of Physics C)
Latex-file available from : subhra@boson.bose.res.in

Coulomb-correlation effects in semiconductor quantum dots: The role of dimensionality

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Abstract

We study the energy spectra of small three-dimensional (3D) and two-dimensional (2D) semiconductor quantum dots through different theoretical approaches (single-site Hubbard and Hartree-Fock hamiltonians); in the smallest dots we also compare with exact results. We find that purely 2D models often lead to an inadequate description of the Coulomb interaction existing in realistic structures, as a consequence of the overestimated carrier localization. We show that the dimensionality of the dots has a crucial impact on (i) the accuracy of the predicted addition spectra; (ii) the range of validity of approximate theoretical schemes. When applied to realistic 3D geometries, the latter are found to be much more accurate than in the corresponding 2D cases for a large class of quantum dots; the single-site Hubbard hamiltonian is shown to provide a very effective and accurate scheme to describe quantum dot spectra, leading to good agreement with experiments.

(Submitted to Phys. Rev. B)
Manuscripts available from: manghi@imoax1.unimo.it

Optimized effective potential method for solids with exact exchange and RPA correlation

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Abstract

We present a new density-functional method which does not exploit the local density approximations (LDA). In this method, we use an exchange-correlation energy which consists of the exact exchange (EXX) and the correlation energies in the random-phase approximation (RPA). A static approximation is used in the evaluation of the functional derivative of the RPA correlation energy. The self-consistent results for solid Cu, Fe, Co, Ni, Si, and MnO (antiferro-II) are presented. For transition metals, Cu, Fe, Co, and Ni, it is shown that the correlation potential gives rise to a large contribution which has the opposite sign to the exchange potential. Resulting eigenvalue dispersions and the magnetic moments are very close to those of LDA's and the experiments. On the other hand, the Fermi contact part of the hyperfine field are rather different from the LDA results, and are in better agreement with the experiments. Obtained band gap for Si is larger than LDA by ~ 0.2 eV. As for MnO, the density of states show good correspondence with XPS+BIS data.

(to appear in J. Phys. Cond. Mat.)
PS file available as `http://ann.phys.wani.osaka-u.ac.jp/~kotani/pap/rpa1.ps.Z`
or `.../pap/rpa1_ps.lzh`
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Optical properties of confined Si structures

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Abstract

The optical properties of bulk silicon are deeply modified if the material is manipulated at the nanometre scale. In particular the growth of Si nanostructures constitutes today one promising approach for the development of silicon-based light emitting devices. In this context I discuss theoretical results on the optoelectronic properties of low-dimensional silicon structures, e.g. Si quantum wells, quantum wires, quantum dots. The results are compared with recent experimental data.

(Accepted by Physica Status Solidi B)
Manuscripts available from: ossicini@imoax1.unimo.it

Optical properties of Si/CaF$_2$ superlattices

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Abstract

We present a first-principle theoretical study of the dielectric functions of Si/CaF$_2$ superlattices. In particular, we investigate how the optical response depends on the thickness of the Si layers. Our results show that for very thin Si slabs (well width less than ~ 20 Å) optical excitation peaks are present in the visible range. These peaks are related to strong transitions between localized states. Moreover the static dielectric costant is considerably reduced. From the comparison made with recent experimental data on similar systems we conclude that the quantum confinement, a good surface passivation and the presence of localized states are the key ingredients in order to have photoluminescence in confined silicon based systems.

(Accepted by Journal of Luminescence)
Manuscripts available from: ossicini@imoax1.unimo.it

Supersoft Transition Metal Silicides

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Center for Computational Materials Science, Wien, Austria

Abstract

Candidates for epitaxially stabilized structures of Fe-, Co- and Ni-silicides are searched by *ab initio* calculations. We find that pseudomorphic phases of $FeSi_2$ in the C1 structure and CoSi and NiSi in the B2 structure soften dramatically under compressive strain induced by epitaxy on a (100) substrate. This supersoft effect is reflected by zero strain energy, constant volume and constant bond energies.

published in: Phys. Rev. Letters **81**, 1969 (1998).
Reprints available from: Raimund.Podloucky@univie.ac.at

Fixed-node DMC for Fermions on a lattice: Applications to the doped Fullerides

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Abstract

Fullerides are crystals made from C_{60} molecules. When doped with alkali metals the valence electrons of the alkali atoms are transfered to the C_{60} molecules. We show how to set up a model Hamiltonian to describe the correlated hopping of these electrons between C_{60} molecules. Then we discuss Monte Carlo methods for such lattice Hamiltonians, putting special emphasis on the optimization of Gutzwiller wavefunctions both in variational and fixed-node diffusion Monte Carlo. As application of these methods we analyze the metal-insulator transition in the integer-doped Fullerides.

Proceedings of the NATO ASI Qunatum Monte Carlo Methods in Physics and Chemistry, July 12-24, 1998, Cornell University, Ithaca, NY
Preprint available at `cond-mat/9808110`

Prediction of Bias-Voltage Dependent Corrugation Reversal for STM-images of bcc-(110)-surfaces: W(110), Ta(110) and Fe(110)

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Abstract

We predict a bias-voltage dependent corrugation reversal for scanning tunneling microscopy (STM) images with atomic resolution of bcc-(110) transition metal surfaces: Atoms which appear usually on STM images of metal surfaces as protrusions, may appear on these images anti-corrugated e.g. as hollow sites and *vice versa* hollow sites may appear as atoms. This makes the absolute determination of atom sites by STM unreliable. We investigate the image-reversal in detail for the W(110) surface and explain its origin on the basis of the electronic structure. We found, the image is determined by a competition between surface resonance states with d_{xz}- and d_{z^2}-character contributing to a direct image of atomic sites and surface-state bands around the $\bar{S}$-point of the two-dimensional Brillouin-zone with *pd*-bonding character and bonding charge between the surface atoms. The surface states contribute to anti-corrugated images. Finally the image depends on the bias voltage. For W(110) and positive bias voltages the surface resonances dominate over the surface states leading to a direct image of atomic sites. For negative voltages below a critical value of -0.4 eV calculations show a reversed image, i.e. anti-corrugation. The critical bias voltage depends slightly on the tip–sample separation. For bias voltages around the critical value corrugating and anti-corrugating contributions to the STM image compensate each other, the corrugation amplitudes become extremely small, the atomic resolution disappears, which is consistent with the experimental difficulties in achieving atomic resolution on W(110) for negative voltages and stripe-like images are predicted. For positive bias voltages we found a good agreement between the theoretical results and our measured STM images. The competition between surface resonances and surface states is a quite general mechanism and anti-corrugation is expected to occur on (110)-surfaces of other bcc transition-metals (i.e. Nb(110), Mo(110), Ta(110)). We demonstrated this explicitly for Ta(110), anti-corrugation occurs practically over the entire bias-voltage range available by a STM and an image-reversal from an anti-corrugated to a corrugated image is predicted for 1.3 eV. For magnetic surfaces the image-reversal may occur twice, once for majority and once for minority states. For Fe(110) we show that the minority spin channel controls the STM image. We predict a direct image for majority states and an anti-corrugated image for minority states below a bias voltage of 0.7 eV, and we predict only one image-reversal at about 0.4 eV for an ordinary non-spinpolarized STM. Employing the full-potential linearized augmented planewave (FLAPW) method in film geometry, the electronic structure is determined by first principles calculations within the framework of the density functional theory in the local (spin) density approximation. The STM analysis is carried out within the s-orbital tip-model of Tersoff and Hamann. An efficient analysis of the corrugation amplitude in terms of two-dimensional star coefficients of the vacuum density of states is presented. The tip-sample distance dependent $\mathbf{k}_{\|}$-point selection to the tunneling current is analysed. The enhancement of the corrugation amplitude due to p_z and d_{z^2}-type tip-orbitals are determined. We show that the enhancement factors calculated are close to the analytical factors given by Chen.

(Accepted at PRB)
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Theory of Pressure Induced Phase Transitions in Cerium Chalcogenides

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Abstract

The electronic structures of the cerium chalcogenides CeS, CeSe and CeTe are studied using the self-interaction corrected local spin-density approximation. This method allows for either a localized or an itinerant description of the cerium f-electrons. The observed equilibrium lattice constants and bulk modulii are well reproduced assuming a trivalent cerium configuration. Pressure induced phase transitions are associated with the delocalization of the f-electrons. The observed transitions are quantitatively reproduced in the calculation, and new high-pressure phase transitions are predicted. The calculations provide a unifying picture of the cerium chalcogenides under pressure.

(Phys. Rev. B.: submitted)
Manuscripts available from: svane@dfi.aau.dk

Excitation spectra of the Ce monopnicitides within Dynamical Mean Field Theory

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Abstract

The excitation spectra of the Ce monopnictides CeN, CeP and CeAs are calculated using a lattice tight-binding model including the local Coulomb repulsion, U, on the Ce $4f$ orbitals. The model is treated within the Dynamical Mean Field Theory, whereby the problem is mapped onto an effective Anderson impurity model. This is solved in a finite-U extension of the Non-Crossing Approximation, including lowest-order crossing diagrams. The lattice model is parametrized by means of *ab initio* calculations. The calculated spectra are in good agreement with experiment. In particular, dispersive quasiparticle peak positions are found close to the Fermi edge in CeP. CeN shows metallic Fermi-liquid behaviour with a correlation-induced mass enhancement factor of ~5 around the Fermi level.

(Phys. Rev. B.: in press)
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Theory of the $\alpha - \gamma$ phase transition in Ce

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Abstract

The Kondo volume collapse model of the isostructural $\alpha - \gamma$ phase transition in elemental cerium is investigated by a combination of the self-interaction corrected local density approximation (SIC-LDA) and the Anderson impurity model. The zero-temperature uncorrelated total energy function as well as the model hybridization parameters are calculated with the SIC-LDA approach, while temperature and correlation effects are calculated within the impurity model, using an extension of the non-crossing approximation. It is found that the phase transition may be quantitatively well described with this approach, provided a rescaling of the hybridization parameters is invoked. The influence of Ce f^2 configurations on the accuracy of the calculations is discussed.

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Di–carbon complexes in AlAs and GaAs

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Abstract

Heat treatment of heavily carbon doped AlAs and GaAs results in a loss of C_{As} shallow acceptors. In Raman scattering experiments on annealed CBE grown GaAs with ^{12}C and ^{13}C isotopes, and MOVPE grown AlAs it is found that the loss of carriers is accompanied by the appearance of two high frequency lines. These lie near to the stretch mode of an isolated C_2 molecule (1855 cm^{-1}). This is consistent with the formation of two types of di-carbon defects in these materials where the C atoms are bonded together and one or both of which act as a donor.

Using a local density functional method to investigate the structure and dynamics of several di-carbon defects, we find that the dimer at an As site is bistable and aligned approximately in a [100] direction in the neutral charge state, and in a [110] direction when positively ionised. The calculated frequencies lie within 10% of the measured values in both materials. Other defects are investigated too with a view of determining the structures giving rise to the modes.

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Postscript file available from C. D. Latham email: C.D.Latham@ex.ac.uk

Nitrogen-hydrogen defects in GaP

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Abstract

Models of the nitrogen-hydrogen defect in GaP, which contain one and two H atoms, are investigated using *ab initio* density functional cluster theory. We find that a single H atom binding to N possesses two infra-red absorption frequencies close to those attributed to an NH_2 defect. The modes shift with its charge state consistent with the photo-sensitivity found for the defect. A third mode observed for this centre is assumed to be an overtone of the bend mode. The isotope shifts of the calculated modes are in excellent agreement with experiment in contrast with the model which contains two H atoms.

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Interaction of oxygen with dislocations in GaN

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Abstract

A review is given of the results of first principles calculations used to investigate the structure and electronic properties of screw and edge dislocations in GaN. These showed that both cores are reconstructed without any deep states. The atoms comprising the wall of the core of the screw dislocation possess heavily strained bonds and there is a reduction in line energy when the first shell of Ga and N atoms is removed, leading to a screw dislocation with a small open core. The interaction of oxygen with the cores of both dislocations is considered and it is found that the impurity has a strong tendency to be bound by Ga vacancies leading to three types of defect trapped in the strain field. We suggest that the most stable defect leads to a poisoning of growth centres on the walls of nanopipes.

(Proceedings of conference on Extended Defects in Semiconductors, Jaszowiec, Poland, September 1998, to appear in Physica Status Solidi)
Postscript file available from R. Jones email: R.Jones@ex.ac.uk

First stage of oxygen aggregation in silicon: the oxygen dimer

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Abstract

The structure and dynamic properties of the interstitial oxygen dimer in silicon are found using a combination of infra-red spectroscopy and *ab initio* modeling. We find the stable dimer consists of a pair of inequivalent weakly-coupled interstitial oxygen atoms separated by a Si-Si bond. Two high frequency modes are decoupled in one ^{16}O-^{18}O combination but are strongly mixed in the other combination. A third lower lying mode involves the compression of the Si-Si bond joining the oxygen atoms and gives distinct modes in the mixed ^{16}O-^{18}O case.

(To appear in Physical Review Letters)
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Effect of oxygen on the growth of $(10\bar{1}0)$ GaN surfaces: the formation of nanopipes

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Abstract

Local density functional methods are used to examine the behaviour of O and O related defect complexes on the walls of nanopipes in GaN. We find that O has a tendency to segregate to the $(10\bar{1}0)$ surface and identify the gallium vacancy surrounded by three oxygen impurities (V_{Ga}–O_{3N}) to be a particularly stable and electrically inert complex. We suggest that during Stranski-Krastanow growth, when inter-island spaces shrink, these defects reach a critical concentration beyond which further growth is prevented and nanopipes are formed.

(To appear in Phil. Mag.)
Postscript file available from R. Jones *e*mail: R.Jones@ex.ac.uk

Deep acceptors trapped at threading edge dislocations in GaN

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Abstract

Local density functional methods are used to examine the behavior of the gallium vacancy, oxygen and related defect complexes trapped at threading edge dislocations in GaN. These defects are found to be particularly stable at the core of the dislocation where oxygen sits two–fold coordinated in a bridge position. V_{Ga}–O_N is found to be a deep double accecptor, V_{Ga}–$(O_N)_2$ is a deep single acceptor and V_{Ga}–$(O_N)_3$ at the dislocation core is inactive. We suggest that the first two defects are responsible for a deep acceptor level associated with the mid-gap yellow luminescence band.

(To appear in Physical Review Letters)
Postscript file available from R. Jones email: R.Jones@ex.ac.uk

Second-moment interatomic potential for Cu-Au alloys based on total-energy calculations and its application to molecular-dynamics simulations

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Abstract

We have evaluated interatomic potentials of Cu, Au and Cu-Au L1 2 ordered alloys in the framework of the second- moment approximation to the tight-binding theory by fitting to the volume dependence of the total energy of these materials computed by first- principles augmented-plane-wave calculations. We have applied this scheme to calculate the bulk modulus and elastic constants of the pure elements and alloys and we have obtained a good agreement with experiment. We also have performed molecular-dynamics simulations at various temperatures, deducing the temperature dependence of the lattice constants and the atomic mean- square-displacements, as well as the phonon density of states and the phonon-dispersion curves of the ordered alloys. A satisfactory accuracy was obtained, comparable to previous works based on the same approximation, but resulting from fitting to various experimental quantities.

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Ab-initio Calculation of Near-Edge Structures in Electron Energy Loss Spectra for Metal-Oxide Crystals I: Oxygen K Edges

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Abstract

The local electronic structure and its relation to the atomic environment of the ions in MgO, $MgAl_2O_4$, and α-Al_2O_3 are analyzed by means of ab-initio band-structure calculations based on the density functional theory. The theoretical results for local densities of states are compared to electron energy loss near edge structures (ELNES) obtained by analytical transmission electron microscopy. The data are decomposed and analyzed with respect to the mutual interaction of the anionic and cationic sublattices. This part I focuses on the oxygen ELNES. The validity of the effective one-electron approximation for the crystal potential and of the perturbative treatment of single-electron excitations is demonstrated quantitatively for the anionic centers.

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Ab-initio Calculation of Near-Edge Structures in Electron Energy Loss Spectra for Metal-Oxide Crystals II: Cation Edges

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Abstract

Based on the theoretical analysis of the local electronic structure in ionic metal-oxide compounds given in the preceding part I, this part II addresses the limitations of the quantitative description of electron-energy-loss near-edge structures (ELNES) at the cationic centers by means of local densities of states. Improvements in the theoretical treatment are illustrated and discussed in comparison to experimental ELNES data. In particular this concerns the explicit account for core relaxation effects in the process of the core excitations, and the inclusion of symmetry constraints on the probabilities for the core-valence excitations.

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Molecular precursors in the dissociative adsorption of O_2 on Ni(111)

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Abstract

The dissociative adsorption of oxygen on the (111) surface of nickel has been studied using ab-initio local-density-functional calculations. A strongly chemisorbed molecular precursor located in a threefold hollow and stretching from top to bridge has been identified. The barrier for dissociation has been calculated using the nudged-elastic-band method and found to be rather modest ($E_{\mathrm{barr}} = 0.2$ eV). Our results are discussed in relation to recent molecular beam experiments and ab-initio calculations for O_2 precursors on Pt(111).

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Reaction channels for the catalytic oxidation of CO on Pt(111)

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Abstract

The oxidation of CO on an oxygen precovered Pt(111) surface has been modelled via ab-initio local-density calculations (including generalized gradient corrections) using the Vienna ab-initio simulation package VASP. Reaction barriers and transition-states are determined using the nudged-elastic-band method. Based on the results from the calculations a complete scenario of subsequent reactions is modelled: starting from a co-adsorption phase of molecular O_2 precursors and on-top adsorbed CO molecules at $\Theta_{O_2} = \Theta_{CO} = 1/4$ half of the O_2 is desorbed ($E_{act} = 0.75$ eV). At this lower coverage dissociation of O_2 and hence a bi-molecular reaction $O_2 + CO \rightarrow CO_2 + O$ becomes possible ($E_{barr} = 0.46$ eV). Finally the atomic oxygen at the surface may further react with CO to form CO_2 ($E_{barr} = 0.75$ eV).

(Proceedings International Surface Science Conference (Birmingham, Sept. 1998), in print)
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CONDUCTION ELECTRON STATES IN GADOLINIUM AT FINITE TEMPERATURE

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Abstract

The conduction electron states in various non-collinear configurations of the 4f moments are studied in the case of Gadolinium. The results of the calculations are used to reveal trends in temperature variation of the conduction electron states. We show that the conduction electron states preserve their spin-polarization at any extent of the disorder of the atomic 4f moments. The induced local atomic moments of the conduction electrons resulting from this polarization appeared to be rather stable. At zero temperature, the effect of spin polarization can be interpreted in terms of the exchange or spin splitting which is the main notion of the Stoner model of itinerant electron magnetism. At finite temperatures, the notion of the spin-splitting becomes ill-defined because of the noncollinearity of the atomic 4f moments. With increasing angles between the 4f moments there is a transition from exchange-split bands to spin-hybridized bands. We have interpreted the experimentally observed features of the temperature dependence of the photoemission and optical spectra of Gd. Seemingly contradictory, these results can be explained within the same theoretical scheme referring to different temperature behavior of different parts of the conduction electron states.

(To appear in "Magnetism and Electron Correlations in Local-Moment Systems: Rare-Earth Elements and Compounds" (Ed. W. Nolting))
A copy of the manuscript can be obtained from:
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9 Presenting Other Initiatives

CCP3: Surface Science

Computational Collaborative Project (CCP) 3 is a network of groups interested in theoretical and computational surface science. It supports activity in the computer simulation of surfaces and interfaces through code development, a regular series of workshops and meetings, and by supporting an extensive programme library. The state of the art computational tools developed within the project are collected in the library and made available to academic researchers. The collaboration is managed by a working group of 26 leading surface scientists and is co-ordinated by CLRC Daresbury Laboratory in England.

CCP3 produces a biannual newsletter. The July 1998 issue contains, amongst others, articles about nanostructures, absorption studies and the potential felt by tunneling electrons.

The newsletter may be dowloaded from the WWW pages at:

http://www.dl.ac.uk/CCP/CCP3

or can be requested as a printed copy by sending e-mail to:

ccp3@dl.ac.uk.

Nicholas M Harrison

10 SCIENTIFIC HIGHLIGHT OF THE MONTH

NOVEL RECONSTRUCTION MECHANISMS: A COMPARISON BETWEEN GROUP-III-NITRIDES AND "TRADITIONAL" III-V-SEMICONDUCTORS

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Abstract

We have studied the driving forces governing reconstructions on polar GaN surfaces employing first-principles total-energy calculations. Our results reveal properties not observed for other semiconductors, as for example a strong tendency to stabilize Ga-rich surfaces. This mechanism is shown to have important consequences on various surface properties: Novel and hitherto unexpected structures are stable, surfaces may become metallic although GaN is a wide-bandgap semiconductor, and the surface energy is significantly higher than for other semiconductors. We explain these features in terms of the small lattice constant of GaN and the unique bond strength of N_2 molecules.

10.1 Introduction

Progress in the materials quality of GaN has led recently to the first commercially available, highly efficient optoelectronic devices emitting in the green and blue/UV region [1, 2]. A substantial problem in growing GaN and its alloys is the lack of a lattice-matched substrate. Bulk GaN can be grown only in small crystallites and sapphire, the most commonly used substrate, has an extremely large lattice mismatch (14%). Another problem is the high nitrogen vapor pressure of bulk GaN requiring highly activated nitrogen precursors for the growth. Both issues make it difficult to grow routinely and in a controlled fashion high quality GaN. In order to overcome these problems it is critical to understand the fundamental growth aspects on an atomic level.

Initially, it has been believed that the driving forces behind surface reconstructions and growth are essentially the same as for conventional semiconductors such as *e.g.* GaAs. However, it soon became obvious that GaN behaves in many aspects very differently. For example, impurity concentrations are significantly higher than in conventional semiconductors and p-type doping is rather difficult [3]. Also, growth is much more affected by even small changes in the growth environment and the structure of the initial nucleation layer at the substrate controls the properties and quality of the entire epitaxial layer.

Recent investigations also revealed surface structures for the technologically relevant polar GaN surfaces which are very different from the well-established structures of III-V semiconductor surfaces. Furthermore, some of these structures disobey well-accepted empirical rules and models, which have been found useful for understanding why and how semiconductor surfaces reconstruct. For example, on cubic GaN (001) (which is commonly used to grow the cubic phase of GaN) first-principles calculations identified a Ga-terminated surface as the energetically most stable structure. On this surface four Ga atoms form linear tetramers [4]. This is in contrast to conventional semiconductors where dimers are the preferred building blocks on (001) surfaces. Another example is the Ga adlayer structure which has been found combining detailed STM and LEED measurements with first-principles calculations at the wurtzite GaN $(000\bar{1})$ surface [5]. This surface violates several rules: It disobeys electron counting, atoms in the top surface layer sit on singly coordinated sites, and each surface atom has the highest possible number of dangling-bond states.

The aim of the present paper is to identify the properties of GaN that give rise to these unusual surface reconstructions, to understand why the empirical rules that have been well established to describe conventional semiconductor surfaces fail for GaN, and to determine whether these rules can be extended to GaN. We will focus here on the *mechanisms* and *general principles* of the surface reconstructions. Detailed descriptions of the specific atomic structures and the calculations for cubic and wurtzite GaN can be found in Refs. [4, 5]. After a brief description of the computational details (Sec. II) we will analyze the surface energies of unreconstructed GaN and GaAs surfaces. Based on these results we show that a characteristic feature of GaN surfaces is the tendency to have Ga atoms in the surface layer. This feature, combined with the small lattice constant, is shown to be responsible for the unusual surface reconstructions. Finally, based on this analysis we derive conclusions concerning possible surface reconstructions.

10.2 Computational method

The energy necessary to create a surface is called the surface energy. This energy is not constant but depends on the specific thermodynamic conditions. Specifically, in GaN the relative concentration of Ga and N atoms at the surface determines the surface energy. The atomic reservoirs with which Ga and N atoms are exchanged in order to modify the surface stoichiometry determines the chemical potentials (μ_{Ga}, μ_{N}). The chemical potentials for Ga and N are not independent variables, since for thermal equilibrium situations both species are in equilibrium with the GaN bulk:

$$\mu_{\mathrm{GaN}} = \mu_{\mathrm{Ga}} + \mu_{\mathrm{N}} \tag{1}$$

The surface energy at $p = 0$ and $T = 0$ is then given by:

$$\gamma = E^{\mathrm{tot}} - \mu_{\mathrm{Ga}} N_{\mathrm{Ga}} - \mu_{\mathrm{N}} N_{\mathrm{N}} \tag{2}$$

where N_{Ga} and N_{N} are the number of Ga and N atoms and E^{tot} is the total energy of the surface obtained from density-functional theory.

The gallium chemical potential can be varied only between certain limits. A major criterion is that the chemical potential for an element is less than the chemical potential of the corresponding bulk material (or molecules) since otherwise this element would form the energetically more stable bulk or molecular structure. For the gallium chemical potential an upper limit is therefore given if GaN is in thermodynamic equilibrium with bulk Ga. This case is called the Ga-rich limit. The lower limit is given for GaN in thermodynamic equilibrium with N_2 molecules; it is therefore called the N-rich limit. Using these relations and Eq. (1) we get:

$$\mu_{\mathrm{Ga(bulk)}} + \Delta H_{\mathrm{GaN}} \leq \mu_{\mathrm{Ga}} \leq \mu_{\mathrm{Ga(bulk)}} \quad . \tag{3}$$

Here, ΔH_{GaN} is the heat of formation which is defined as:

$$\Delta H_{\mathrm{GaN}} = \mu_{\mathrm{GaN(bulk)}} - \mu_{\mathrm{Ga(bulk)}} - \mu_{\mathrm{N_2(molecule)}} \quad . \tag{4}$$

A negative heat of formation means the reaction is exothermic. The corresponding bulk chemical potentials are calculated from the bulk forms of Ga metal (orthorhombic), N (N_2 molecule) and GaN (wurtzite). The total energies have been calculated employing density-functional theory in the local density approximation, in combination with a plane-wave basis set and first-principles pseudopotentials. The exchange and correlation energy functionals are those derived from the homogeneous electron gas calculations of Ceperley and Alder [7]. We use soft Troullier-Martins [8] pseudopotentials constructed with the fhi98PP package [9]. An explicit treatment of the Ga $3d$ electrons as valence electrons has been found crucial to calculate accurate surface energies. This required a large plane wave energy cutoff making our calculations computationally rather challenging both with respect to CPU-time and memory demand. We therefore used a parallel version of our plane wave code on a Cray T3E. This version had been specifically optimized with respect to data and CPU partitioning. Details about the program can be obtained from Ref. [10].

10.3 Analysis of the surface structures

As pointed out in Sec. 1, surface reconstructions of GaN exhibit features that have not been observed on other III-V semiconductor surfaces. In order to identify the mechanisms causing the unusual reconstruction we will analyze the differences between polar GaN and GaAs surfaces. We will focus on polar surfaces since non-polar surfaces show essentially the same features as found for conventional semiconductors [14]. Since we are here interested in the mechanisms driving surface reconstructions on GaN surfaces let us first briefly recall the rules and models that are typically applied in a discussion of conventional semiconductor surfaces. A commonly used principle is called the electron counting rule (ECR). According to the ECR the equilibrium surface is one in which the number of available electrons in the surface layer will exactly fill all dangling-bond states in or near the valence band and leave all states in or close to the conduction band empty [11]. An important consequence of this rule is that a surface satisfying the ECR will be semiconducting. Further, just by counting electrons and dangling-bonds a large number of potential surface structures can be eliminated. While this rule is empirical, it has been found to work well for almost all conventional semiconductor surfaces. Only a few exceptions have been reported [16, 20].

The ECR is commonly justified in terms of Harrison's bond-orbital model [12]. Atoms in conventional semiconductors are sp^3 hybridized. In the absence of reconstruction some of the hybrid orbitals cannot form bonds, but instead give rise to partially occupied sp^3 dangling-bond states. According to Harrison the energy levels of the cation dangling-bond states are high in energy (lying close to or within the conduction band) and should therefore be empty. Dangling bond states localized on the more electronegative anions, however, are close to or within the valence band and should be filled. Other mechanisms driving the reconstruction at semiconductor surfaces are: (i) the tendency to reduce the number of dangling bond states on the surface by forming e.g. dimers, adatoms or trimers [20, 21] and (ii) minimizing the electrostatic energy by optimizing the arrangement of charged surface atoms [13].

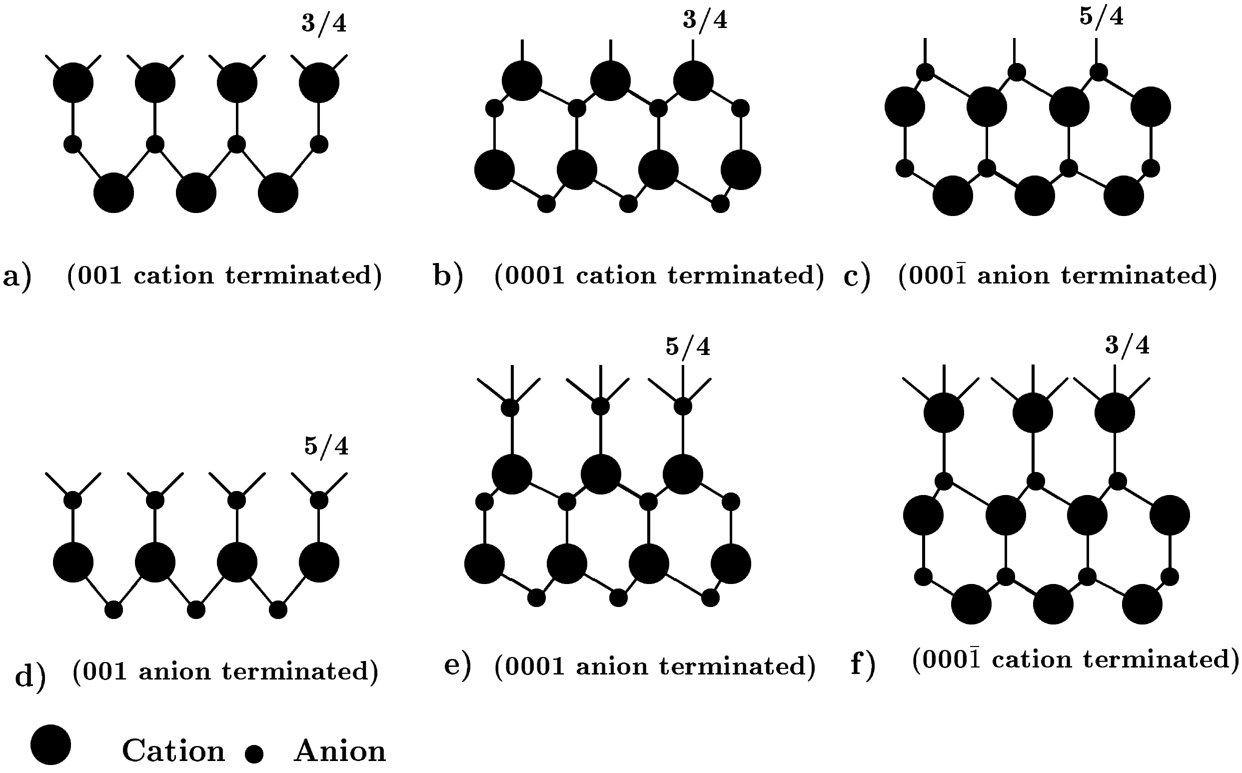
10.3.1 Reconstruction mechanisms for "traditional" semiconductors

We will start our comparison between GaAs and GaN by considering the simplest possible surface structures - the unreconstructed (1x1) surfaces. These surfaces (Fig. 1) are terminated either by cations or by anions. For GaAs possible structures are the open (001) surface and the close-packed (111) (cation-face) and $(\bar{1}\bar{1}\bar{1})$ (anion-face) surfaces. Since the equilibrium phase of bulk GaN is the wurtzite structure we performed the calculations for (0001) (cation-face) and $(000\bar{1})$ (anion-face) which are equivalent up to the fourth nearest neighbors to the cubic (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces. Since we are here only interested in qualitative aspects, we will consider the $(111)/(\bar{1}\bar{1}\bar{1})$ and $(0001)/(000\bar{1})$ as equivalent surfaces.

10.3.2 Comparison between unreconstructed GaAs and GaN surfaces

The calculated surface energies of GaAs are plotted as a function of the chemical potential in Fig. 2 (a-c)[27]. The energies are fully consistent with the empirical rules and models discussed above. First, both Ga and As-terminated (1x1) surfaces have much higher surface energies than the reconstructed equilibrium surfaces implying that the (1x1) surfaces are unstable against surface reconstruction. This is consistent with the fact that all possible polar (1x1) surfaces have partially occupied dangling bonds and thus disobey electron counting. Further, consistent with the principle of reducing the dangling bond density, both the Ga-terminated (111) and the As-terminated $(\bar{1}\bar{1}\bar{1})$ surfaces that have only *one* dangling bond orbital per surface atom (see Fig. 1b and 1c) are energetically more stable than the corresponding As and Ga-terminated surfaces that have *three* dangling-bond orbitals per surface atom.

For GaN (Fig. 2, d-f) some of these mechanisms are no longer valid. First, N-terminated surfaces are energetically always less stable than the corresponding Ga-terminated surfaces. This result applies even for the $(000\bar{1})$ surface where the Ga-terminated surface has three (Fig. 1f) and



a) (001 cation terminated) b) (0001 cation terminated) c) (000$\bar{1}$ anion terminated)

d) (001 anion terminated) e) (0001 anion terminated) f) (000$\bar{1}$ cation terminated)

Figure 1: Atomic structures for the low index (001), (0001) [which is equivalent to (111)] and (000$\bar{1}$) [which is equivalent to ($\bar{1}\bar{1}\bar{1}$)] surfaces of III-V-semiconductors. The numbers give the electrons per dangling-bond orbital.

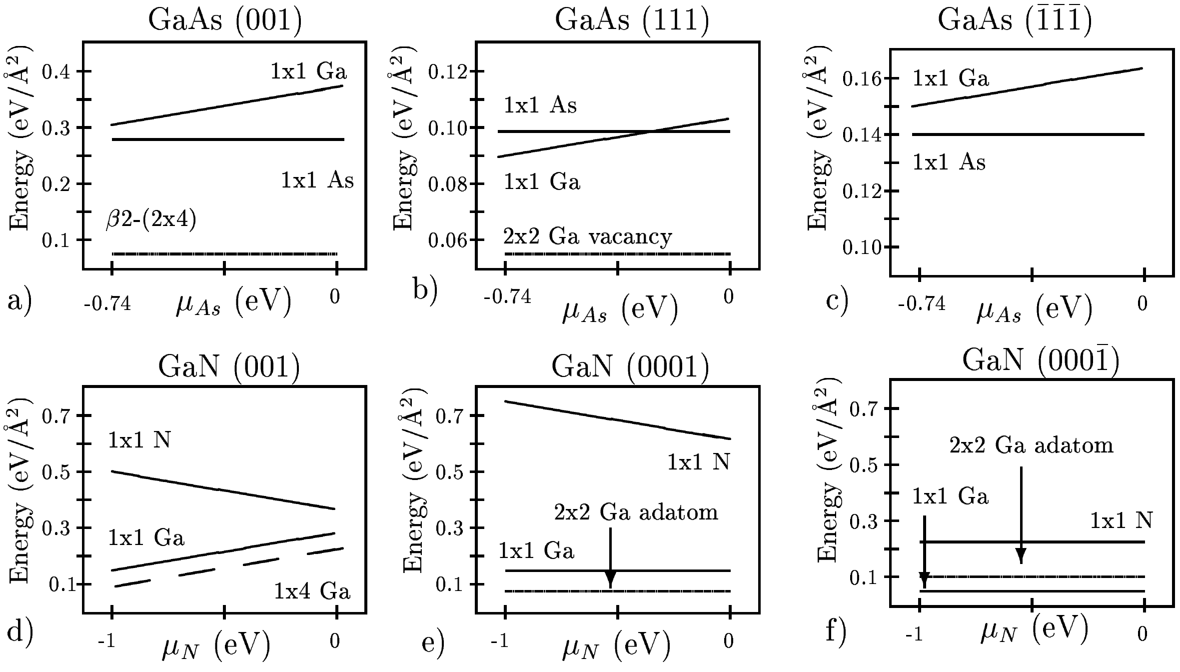


Figure 2: Surface energies in eV/Å^2 for the cubic (001), (111) and ($\bar{1}\bar{1}\bar{1}$) GaAs and the (001), (0001) and (000$\bar{1}$) GaN surfaces (solid lines). Note that both the unreconstructed Ga and As terminated surfaces are very high in energy compared to the equilibrium surfaces (dashed lines).

Element	Zn	Al	Ga	In	N	P	As	O	S	Se
E_{coh} (eV)	1.35	3.42	2.81	2.52	4.91	3.28	2.96	2.58	2.87	2.35

Table 1: Experimental cohesive energies and molecule binding energies (N_2 and O_2) of the constituent species in common semiconductors [15].

the N-terminated surface only one dangling bond orbital per surface atom (Fig. 1c). Second, the Ga-terminated surfaces have a very low surface energy, which is only slightly higher than the surface energy of the reconstructed equilibrium surfaces. This is in clear contrast to GaAs where all unreconstructed surfaces are much higher in energy than the equilibrium structures. In fact, for $(000\bar{1})$ the Ga-terminated (1x1) structure (Fig. 1f) becomes the energetically preferred structure under Ga-rich conditions (see Fig. 2f). This structure, however, obviously disobeys the electron counting rule.

10.3.3 Reconstruction mechanisms on GaN surfaces

From these results we can immediately conclude that a major mechanism driving GaN surface reconstructions is the tendency to stabilize structures that have more Ga than N atoms in the surface layer. This conclusion is also consistent with recent experimental and theoretical studies on GaN surface reconstructions [5]. Almost all equilibrium surfaces consist solely of Ga atoms in the top surface layer. The only exception for polar surfaces is the (0001) surface, where under nitrogen-rich conditions N-adatoms can be stabilized on a Ga-terminated surface [5, 26]. This feature of preferring just one species in the top surface layer (independent on the chemical potentials) is unique to GaN and has not been reported for other semiconductor surfaces. We will therefore attempt to elucidate the mechanisms responsible for the stabilization of Ga atoms in the surface layer. According to Eq. (2) we can seperate the surface energy into two contributions: (i) the energy necessary to remove or add atoms to the chemical reservoirs (which describe the specific growth conditions) and (ii) the total energy which is the sum over all bond energies and includes contributions such as charge transfer, electrostatic energy etc.

10.3.4 Chemical Potentials

Let us first focus on the chemical potentials. A lower limit on the energy necessary to remove atoms from a chemical reservoir is the bulk cohesive energy for solids and the binding energy per atom for molecules. These energies are shown in Tab. 1 (taken from Ref. [15] for a selected number of elements). The elements have been chosen to be the constituent species of the major semiconductor materials. Let us exclude for a moment group IV elements which will be discussed at the end of Sec. 4.1. Among group II, III, V, and VI elements nitrogen is obviously the element with the highest binding or cohesive energy: The N-N bond in the N_2 molecule is one of the strongest bonds found in nature. All other atoms have energies roughly between 2 - 3 eV, i.e. more than 2 eV less than a N atom in the N_2 molecule. We can therefore conclude that for all compound semiconductors (except for group III-Nitrides) there are only modest differences in the chemical potentials. For group III-nitrides, however, there is a strong asymmetry in the chemical potentials: More energy is required to transfer N atoms from the N reservoir to the surface than to transfer Ga atoms to the surface.

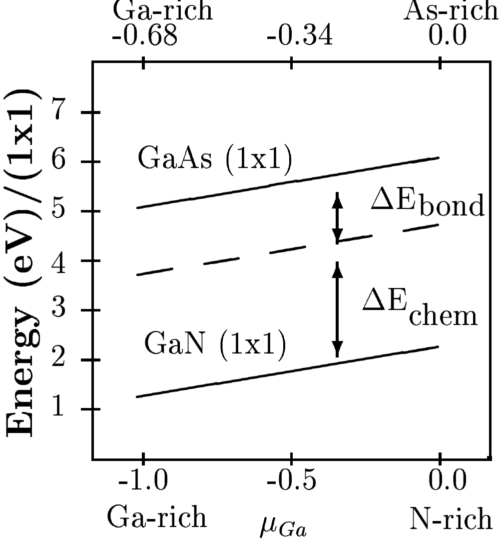


Figure 3: Surface energies for the unreconstructed Ga-terminated GaN and GaAs surfaces as a function of the Ga chemical potential. The dashed line corresponds to the Ga-terminated GaN surface where the difference between the Ga and N chemical potentials has been eliminated by artificially shifting the Ga chemical potential.

A rough estimate of how this asymmetry affects the energy of the GaN surfaces can be obtained by artificially eliminating the large difference in the chemical reservoirs for Ga and N. We therefore shift the Ga-chemical potential by the difference between the N and Ga chemical potential (2.1 eV). The energy to remove a Ga atom is then the same as removing a N atom from its chemical reservoir. The corresponding surface energy is shown in Fig. 3 as dashed line [27]. The energy significantly increases (by ΔE_{chem}) bringing the surface energy closer to that of GaAs.

10.3.5 Metallic bonding

The fact, that ΔE_{chem} gives only 2/3 of the difference with respect to the GaAs surface energy (Fig. 3) indicates that the difference in chemical potentials is not sufficient to explain the unusual stability of the Ga-terminated surfaces at GaN. It is also determined by the binding energy an atom gains if it is incorporated in the surface. The different binding energies on both surfaces can be mainly understood by the formation of second nearest neighbor bonds between surface Ga atoms. This effect can be roughly estimated by calculating the formation energy of a free-standing Ga layer at different lattice constants. The resulting energies shown in Fig. 4 reveal two interesting aspects: First, the equilibrium lattice constant of the free-standing Ga layer is close to the lattice constant of GaN bulk. Therefore, the energy the Ga-layer gains when relaxing from the GaN-bulk lattice constant to its ideal value is modest (0.2 eV). This feature implies that at GaN surfaces the Ga atoms can form metallic bonds similar to those in bulk Ga even without any relaxation. Second, by going from the GaAs bulk lattice constant to the GaN lattice constant the binding energy of the free-standing Ga layer significantly decreases (by 0.9 eV). This energy gain explains largely the stronger bonding energy (ΔE_{bond} in Fig. 3) of Ga atoms on the GaN surface. The energy reduction obtained by contracting the lattice constant

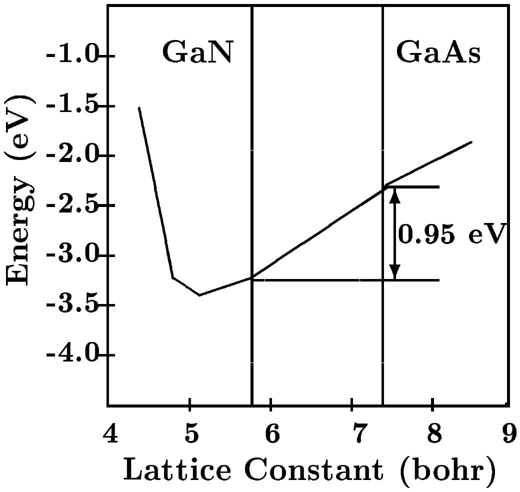


Figure 4: Energy in eV per atom of a free-standing Ga layer as a function of the lattice constant. The energy zero refers to a Ga atom. The dashed lines mark the lattice constants of GaN and GaAs. Obviously, the GaN lattice constant is very close to that of optimum Ga-Ga interaction explaining the stabilization of a Ga adlayer found at GaN surfaces.

of a Ga adlayer from the GaN-bulk value to the equilibrium value has been invoked to explain the stability of a laterally contracted incommensurate Ga-adlayer structure on the GaN(0001) surface[23].

10.3.6 Chemical trends

The above discussion explains the preference for having exclusively one species in the surface layer and the tendency to stabilize structures with low-coordinated configurations that are not observed for conventional III/V semiconductor surfaces. For these materials, the surface atoms prefer three-fold coordinated configurations (i.e. surface atoms have a maximum of one dangling bond) and the dominant surface species changes when going from cation to anion-rich conditions. Based on the cohesive energies shown in Tab. 1, we expect similar features (preference of one species, low-coordinated sites) for the other group III-nitrides (InN, AlN) and also for SiC.

10.4 Surface reconstructions on GaN surfaces

The arguments given above are general and apply to any polar GaN surface, because specific differences between the various surface orientations were not used. However, as can be seen in Fig. 1 the local configuration and the number of nearest neighbor bonds at the surface atoms depend strongly on the surface orientation: for the (001) surface the atoms are two-fold coordinated while for the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces they form one or three bonds. We will therefore elucidate in the following how these specific arrangements affect surface reconstructions and compare with reconstructions found on GaAs.

10.4.1 The cubic GaN (001) surface

We will start with the cubic (001) surface. For GaAs, a detailed analysis of STM measurements by Pashley [11] revealed a set of rules which determine the reconstructions of equilibrium surfaces: Surfaces form (2xN) reconstructions where the 2x periodicity arises from the formation of dimers and the N periodicity arises from the missing surface dimers. These rules combined with the electron counting rule largely restrict the number of possible surface structures. Northrup and Froyen added later the principle of minimizing the electrostatic energy and identified the (2x4)-β2 surface (which obeys all the rules) to have the lowest energy under moderately As-rich conditions [13].

In general, dimers are considered to be the natural building block of surface reconstructions on (001) surfaces and have been observed also for other materials (e.g. AlAs, Si, SiC). The formation of surface dimers is energetically favorable since it reduces the number of dangling bond states by a factor of two. More important, due to the specific arrangement of the atoms on the (001) surface dimers can be formed simply by rotating the back bonds of the surface atom without stretching them (see Fig. 5a). While it is apparent that the formation of dimers is energetically preferred over the unreconstructed surface, it is by no means obvious why other building blocks than dimers should not be formed. Looking at the driving forces for dimers these alternative 'building blocks' should further reduce the number of dangling bonds without significantly stretching the back bonds of the surface atoms. The simplest way to do this is to form 'n-mers' instead of dimers where n surface atoms form a linear chain (an example for n = 4 is shown in Fig. 5b). The number of dangling bonds is then reduced by a factor of $2n/2$ = n where $2n$ is the number of dangling bond states at the unreconstructed surface and 2 the number of dangling bond states per "n-mer". For a dimer we obtain thus a factor of 2 while for a tetramer as shown in Fig. 5b a factor of 4 is achieved: Using these building blocks the number of dangling bonds at surfaces can be much more efficiently reduced than by forming dimers. The tetramer structure as shown in Fig. 5b has also another remarkable feature. It obeys electron counting (each of the three bonds in the tetramer holds 2 electrons and the two remaining dangling bonds are empty/filled if the tetramer consists of cations/anions). Thus, in contrast to the dimer structures, which require a combination of dimers and missing dimers in the surface unit cell, a (1x4) unit cell with a single tetramer is already sufficient to fulfil the ECR.

We have therefore performed calculations for a Ga tetramer on GaAs and GaN. For GaAs we find that a tetramer structure is unstable: without any barrier it spontaneously dissociates into two dimers. The reason for the instability becomes obvious when looking at the geometry as shown in Fig. 5c. In order to form the Ga-Ga bonds in the tetramer the back bonds of the outer atoms (marked by dashed lines) have to be stretched by more than 20% implying that these bonds are virtually broken. For GaAs, the elastic energy necessary to create the tetramer is larger than the energy gained by reducing the dangling bond density. For GaN, however, our calculations reveal Ga tetramers to be lower in energy than a structure consisting of two dimers. In fact, detailed calculations for a large set of possible surface geometries (including those stable on GaAs surfaces) revealed that the tetramer structure is actually the energetically preferred structure [4]. From Fig. 5b we see that the Ga-Ga bonds in the tetramer can be formed almost without stretching the back bonds of the outer atoms: The length of the back

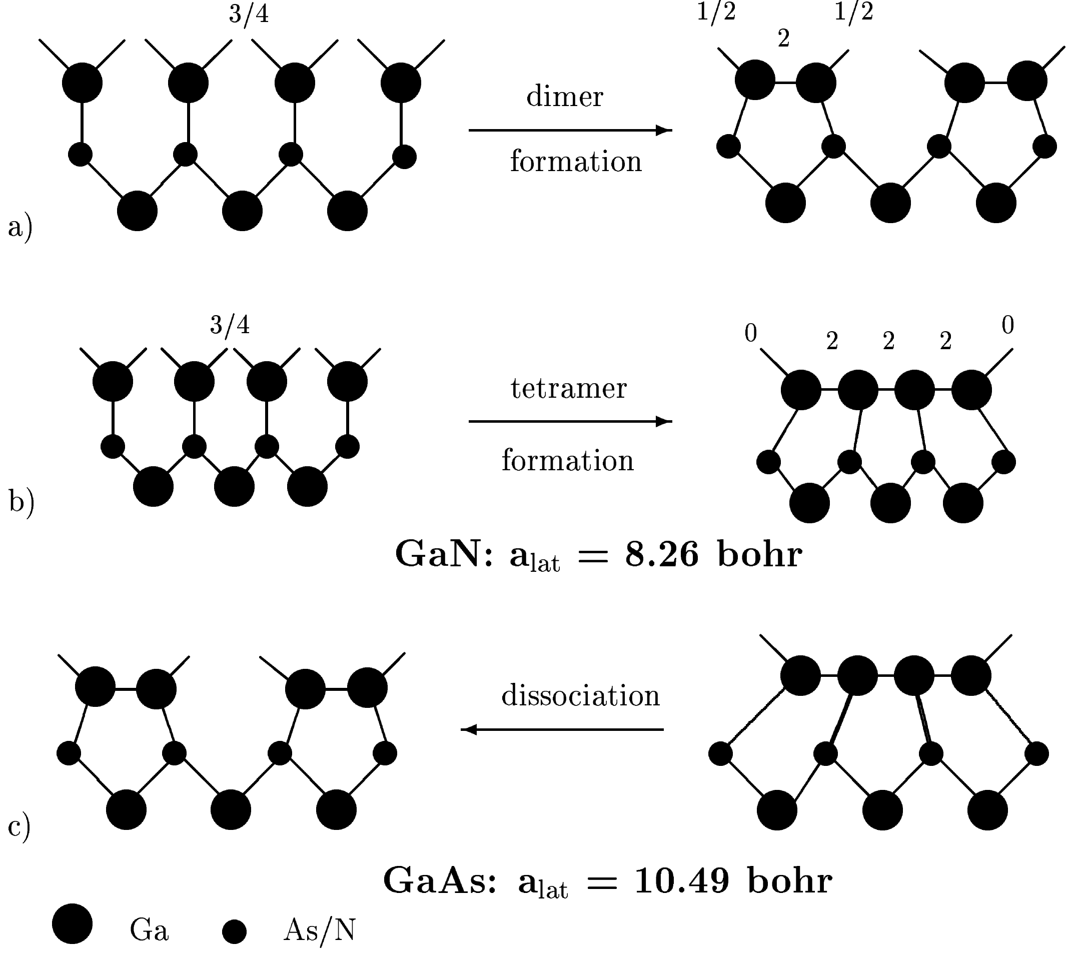


Figure 5: Schematic view of the reconstruction mechanisms of the GaN and GaAs (001) surfaces. Note the difference between the lattice constants of GaN and GaAs which leads to a completely different reconstruction mechanism for the two materials.

bonds increases only by 5% compared to the unreconstructed surface. The reason is simply given in terms of geometric ratios. Since the Ga-Ga bond length remains largely independent of whether the bonds are formed on GaAs or GaN, the stretching of the back bonds and thus the elastic energy becomes smaller with decreasing lattice constant (see also Fig. 5b). This explains why tetramers are stable on GaN (a_{lat} = 8.49 bohr) but not on GaAs (a_{lat} = 10.4 bohr). Based on these arguments we expect very similar structures for the other group III-nitrides (AlN, InN).

10.4.2 The closed packed (0001) and (000$\bar{1}$) GaN sufaces

We will now focus on reconstructions on the close-packed cubic (111) and ($\bar{1}\bar{1}\bar{1}$) structures which are equivalent up to 4th nearest neighbors with the wurtzite (0001) and (000$\bar{1}$) surfaces. A main difference of these surfaces with respect to the (001) surface discussed above is the hexagonal symmetry (C_{3v}) and the lack of a preferred axis along which dimers can be formed. Consequently, the formation of dimers always destroys the point group symmetry of the surface. In fact, dimer geometries have never been reported for these surface orientations. Experimental and theoretical studies showed that surface structures are commonly characterized by the formation of adatom, trimer and vacancy structures [20]. These structures are usually formed in a (2x2) surface unit cell and can be shown to obey electron counting [21].

Let us now consider the GaN (0001) surface. As has been pointed out in Sec. 3 the energetically preferred (1x1) structure is the Ga-terminated surface with one dangling bond state per surface atom (Fig. 1c). This structure is compatible with the principles of having mainly Ga-atoms in the surface and a low dangling bond density. However, first principles calculations showed that this structure is not stable: (2x2) adatom structures that satisfy the electron counting rule are lower in energy [5, 26]. These results are also consistent with recent STM investigations, where mixtures of Ga and N adatoms on these surfaces and semi-insulating behavior have been found [22].

For GaN $(000\bar{1})$ the tendency to prefer Ga atoms in the surface layer prevails over all other principles. A Ga-terminated (1x1) structure becomes energetically most stable despite having a maximum number of dangling bonds (three per surface atom) and clearly disobeys electron counting (Fig. 1f). Similarly, on the AlN $(000\bar{1})$ surface a (1x1) Al-adlayer becomes stable under Al-rich conditions [24].

10.5 Conclusions

Based on first-principles calculations we have studied the driving forces governing surface reconstructions on GaN. The principal mechanisms are (i) the tendency to stabilize Ga atoms in the surface layer, (ii) to obey electron counting and (iii) to reduce the number of dangling bonds. While (ii) and (iii) are well-known mechanisms driving surface reconstructions on other semiconductor materials (i) is a unique property of GaN, and more generally of all group-III-nitrides. The strong tendency to stabilize Ga-rich surfaces is not only a new property without any analogue among other compound semiconductors but it also prevails over the other principles. The most extreme example is the (1x1) Ga-adlayer structure shown in Fig. 1f. This is a metallic structure [5, 23] in which the number of dangling bonds is maximized.

These rules are of course too simplistic to derive *a priori*, i.e. without input from experiment or without performing realistic calculations. However, despite their simplicity these rules have been very successful in explaining or identifying surface reconstructions for a wide range of semiconductors. The knowledge of these mechanisms is not only important to derive conclusions concerning surface reconstructions but also about other properties of the surface. For example, an immediate consequence of the fact that polar GaN surfaces consists mainly of Ga atoms is a decreasing surface energy when going from N-rich to Ga-rich conditions (see Eq. (2)). This might explain why the surface morphology of GaN appears to improve when growing under more Ga-rich conditions [18, 19]. It also explains the exceptionally low diffusion barriers of Ga adatoms on these surfaces (0.2 - 0.6 eV) compared to barriers of 1.5 eV on GaAs [19]: Since the surface layer is comprised mainly of Ga atoms, the Ga adatom forms primarily Ga-Ga bonds which are weak compared to the Ga-N bond (metallic Ga melts already at room temperature). In breaking these bonds to jump from one adsorption site to the next, the Ga adatom must therefore overcome only a small energy barrier [25].

As has been pointed out in detail in Sec. 3 the origin of the stability of Ga-rich surfaces is (i) the large difference in the energies of the chemical reservoirs and (ii) a significantly smaller lattice constant compared to conventional III/V compound semiconductors. We expect therefore a very similar behavior for the other group III-nitrides, i.e. AlN and InN and their alloys.

10.6 Acknowledgements

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