Ψ_k Newsletter

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

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Contents

1 Editorial

In the **General News** section we give some preliminary information on the next Psi-k Conference, Psi-k 2000. In the section **News from the ESF Programme**, apart from reports on collaborative visits, readers will find a report on the *High Pressure Workshop* that took place in Daresbury last December. The report contains abstracts of all presented papers. There are more abstracts in the usual **Abstracts** section. All information on the available positions can be found in the section **General Job Announcements**. Additionally, there is a TMR position announcement in the section **News from the TMR1 Network**. In the section **News from the TMR2 Network** we have an announcement of the *FPLAPW Workshop* that will take place in Vienna on April 7-10, 1999. The scientific highlight by *I.S. Duff (RAL)* is on **"Matrix Methods"**. It is concerned with large-scale applications where matrices are large and sparse. Finally we would like to encourage our readers to check the table of content for more details.

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

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2 General News

2.1 Psi-k 2000 Conference

Psi-k2000 Conference, Schwäbisch Gmünd, 22-26 August, 2000

”Ab initio Electronic Calculations for Elucidating the Complex Processes in Materials

The preliminary information on the Psi-k2000 Conference is available on the Psi-k Network web site. A rough guide for the deadlines for registration, abstracts, conference fee, etc., can be found there and is to be updated in the due course. It is envisaged that all members of the three networks involved in organizing this conference will actively contribute in making it a success. The format of the conference will follow closely that the previous conference, with three parallel sessions, four plenary talks, and many invited talks, to reflect a very high standard of research in the field of the conference. All contributed papers will be accepted as either 10 minute contributed talks or posters. The preference in the former shall be given to young people. It is hoped, that as in the case of the first Psi-k Conference, also many scientists from outside Europe will participate.

Concerning the topics of the conference, it is intended to cover all *ab initio* work as represented by the interest groups of the three European networks that are involved in organising this conference. They range from a variety of methologies to specific applications, involving also real industrial collaborations. Namely

- Methods going beyond LDA
- Plane-wave based techniques
- FLAPW + other full potential techniques
- Order(N) + TB
- Scattering techniques (KKR, LMTO)
- Treatment of f-electrons in materials
- Superconductivity
- Excitations
- Magnetism and magnetic materials

- Surfaces, reactions and catalysis
- Minerals and compounds
- Mechanical properties
- Semiconductors
- Molecular materials
- Nanostructures and nanotechnologies
- Oxide materials
- Spectroscopies

PROVISIONAL TIMETABLE

March	1999	First circular on the WWW
October	1999	Second circular, suggestions for symposia and invited speakers
December	2000	Deadline for suggestions
March	2000	Third circular, details on symposia and speakers
May	2000	Deadline for submission of abstracts and registration
June	2000	Final programme
September	2000	The Conference

3 News from the TMR1 Network

"Interface Magnetism"

3.1 Workshop Announcements

3.1.1 Dichroism Workshop

Hands-On Dichroism Course

26th April - 1st May
Daresbury Laboratories

Supported by TMR1 (Interface Magnetism)

First Announcement

This is a hands-on course on the use of the one-electron codes to calculate the dichroism spectra in the absorption. It will give preference to experimentalists. The purpose of the course is to teach how to use the self-consistent bandstructure codes to generate the one-electron potentials for the calculation of dichroism spectra. This course will last one week. Morning sessions will be dedicated to lectures on the theory and the programs. In the afternoon sessions calculations will be performed in teams consisting of two students (i.e. experimentalists) and one teacher (theoretician). Prospective participants are asked to suggest beforehand a system which he/she would like to study during the course.

Speakers will include:

- M.S.S. Brooks (Karlsruhe)
- H. Ebert (Munich)
- P. Strange (Keele)
- B.L. Györffy (Bristol)
- P. Weinberger (Vienna)

For further informations contact:

Martin Lüders,
Daresbury Laboratories,
Warrington WA4 4AD, UK
e-mail: mlu@dl.ac.uk

Limited funds are available from the TMR1 network on 'Interface Magnetism'.
Updated information can be found on the homepage of Psi-k:

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

3.2 Job Announcement

Post-doctoral Position

Condensed Matter Theory

Strasbourg, France

Applications are invited from European Union nationals, excluding French residents, for the above post funded by a European Training and Mobility Award, supported by the TMR network "Interface Magnetism". The appointment will be funded for a period of one year, extendable on mutual agreement. The successful applicant would be expected to work on the development of Real-Space *ab-initio* band structure method as LMTO or KKR and application to interface and thin film magnetism, under the supervision of Dr H. Dreyssé. Some experience in electronic structure calculations is essential. The salary will be on the Research Assistant scale, according to French regulations. Interested candidates should contact Prof. Dreyssé for further information and send a C.V. with names of two references.

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4 News from the TMR2 Network

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

4.1 Workshop Announcements

4.1.1 FPLAPW Workshop

Fifth WIEN Workshop

Full-Potential LAPW calculations with the WIEN97 code

April 7-10, 1999
Vienna University of Technology, Austria
Chairman: Karlheinz Schwarz (TU-Vienna)
Email: kschwarz@email.tuwien.ac.at

Supported by TMR2 (LAPW) and ESF Program STRUC-Ψ_k.

First Announcement

This workshop (within the Psik network) is concerned with recent progress in density functional calculations using the full-potential Linearized Augmented Plane Wave (FP-LAPW) method as embodied in the WIEN97 code (or related topics).

The workshop will be organized (in two parts) as follows:

- Part I:
  - A short introduction to the LAPW method and the density functional theory
  - Introduction to the use of the WIEN97 program package
  - Hands-on experience
- Part II:
  - New features in WIEN97
  - Results obtained with LAPW (WIEN97) and related topics
  - Discussion and exchange of experience
  - Poster session

Conference site:
The conference will take place at the TU Wien (Vienna University of Technology)
A-1040 Vienna, Wiedner Hauptstr. 8-10, second floor (yellow tower, lecture hall 8)

Contact:

For further information look at our WWW-homepage
http://www.tuwien.ac.at/theochem/wien97/ws99/
or send an email to kschwarz@email.tuwien.ac.at.

5 News from the ESF Programme

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

5.1 Reports on Workshops

5.1.1 Daresbury High Pressure Workshop

Workshop on

" Materials Under Pressure: From Ices to Metals"

Daresbury Laboratory, UK

December 17-18, 1998

Supported by UK's CCP9, ESF and TMR2
Program STRUC-Ψ_k (Electronic Structure Calculations for elucidating the complex atomistic behaviour of solids and surfaces)

The workshop was attended by more than 30 scientists from the UK, Germany, Sweden and Denmark. The purpose of the workshop was to review the recent experimental developments on synchrotrons and neutron facilities which 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 workshop therefore aimed to increase the dialogue between experimentalists and theoreticians.

The range of materials covered by the workshop was truely breathtaking, ranging from studies of elemental metals and intermetallics, to minerals and molecular systems such as ices. Each of these systems were covered by both theoretical and experimental talks. Plenty of time was set aside for the lively discussions, which undoubtely will generate new collaborations between the experimental and theoretical work.

PROGRAMME

Thursday 17 December 1998

10:00 10:30	Coffee
10:30 11:15	Review Talk Metals (Theory): Borje Johansson (Uppsala)
11:15 11:45	Discussion
11:45 12:15	Rajeev Ahuja (Uppsala): Structural Phase Transitions in Alkali metals, Alkaline earth metals and Alkali Hydrides and Halides
12:15 12:30	Discussion
12:30 14:00	Lunch
14:00 15:45	Malcolm McMahon (Edinburgh): X-ray diffraction studies of alkaline and lanthanide metals at high pressure
14:45 15:15	Discussion
15:15 15:45	Helmut Olijnyk (Oxford): Vibrational spectroscopy of metals and molecular crystals at high pressure
15:45 16:00	Discussion
16:00 16:30	Coffee
16:30 17:00	Axel Svane (Aarhus): Self-interaction corrections in the electronic structure theory of lanthanides
17:00 17:15	Discussion
17:15 17:45	Karl Syassen (Stuttgart) New crystal structures of elemental metals under pressure
17:45 18:00	Discussion

Friday 18 December 1998

9:00 9:45	Dominik Marx (Stuttgart) Ab Initio Simulations of Materials under High Pressure
9:45 10:15	Discussion
10:15 10:45	Stewart Clark (Durham) High pressure structure of methanol and ethanol
10:45 11:00	Discussion
11:00 11:30	Coffee
11:30 12:15	John Finney (UCL) Structures, disorder, and metastability in ices at medium pressures

12:15 12:45	Discussion
12:45 13:45	Lunch
13:45 14:30	John Loveday (Edinburgh) High-pressure structural studies of ice and ices
14:30 14:45	Discussion
14:45 15:15	Martin Dove (Cambridge) High-pressure behavior of minerals
15:15 15:30	Discussion
15:30 16:00	David Sherman (Bristol) Chemical bonding and Electronic transitions in the Earth's Deep interior
16:00 16:15	Discussion
16:15	Coffee and Discussion on Future Meetings

Participants

Graeme Ackland	Edinburgh
Rajeev Ahuja	Uppsala
Thiti Bovornratanaraks	Edinburgh
Mike Brooks	Karlsruhe
Stewart Clark	Durham
Klaus Doll	Daresbury
Martin Dove	Cambridge
John Finney	UCL
Gonzalo Gutierrez	Uppsala
Malcolm Guthrie	Edinburgh
Ceri Jenkins	Daresbury
Andrew Jephcoat	Oxford
Borje Johansson	Uppsala
Konstantin Kamenev	Warwick
John Loveday	Edinburgh
Dominik Marx	Stuttgart
Malcolm McMahon	Edinburgh
Derek Middlemiss	Durham
Ian Morrison	Salford
Richard Nelmes	Edinburgh
Helmut Olijnyk	Oxford
Stewart Reed	Edinburgh
Keith Refson	Oxford
David Sherman	Bristol
Paul Strange	Keele
Axel Svane	Aarhus
Karl Syassen	Stuttgart
Dzidka Szotek	Daresbury
Walter Temmerman	Daresbury
R.K. Thapa	Daresbury
Carine Vanpeteghem	Edinburgh

Review Talk: Metals (Theory)

Borje Johansson (Uppsala University, Sweden)

The crystal structure of the elemental metals at ambient conditions will be reviewed. The present theoretical understanding of the structures of the 3d, 4d, and 5d transition elements will be presented. Also the structures of most of the 4f elements can be explained within the same picture. Cerium, however, does not at all fit into this picture and a radically new concept is needed to explain its behaviour. Also Pr and Nd become anomalous at high compressions (pressures of the order of several hundred kilobars). Considerations of the crystal structures of the actinide metals clearly show the dominant role played by the 5f electrons in the bonding of these elements. For the heavier actinides, however, a standard rare-earth-like behaviour is expected, in agreement with experiments. The crucial importance of high pressure experimental investigations for the development of a proper understanding of the atomic ordering in solids is strongly emphasized.

Structural Phase Transitions in Alkali metals, Alkaline-earth metals, Alkali Hydrides and Sodium Halides

Rajeev Ahuja (Uppsala University, Sweden)

We have investigated the structural phase transitions in alkali metals, alkaline-earth metals, alkali hydrides and sodium halides theoretically under high compressions by means of first-principles self-consistent total-energy calculations within the local-density approximation using the full-potential linear-muffin-tin-orbital (FPLMTO) method. Our results confirm the recent high pressure experimental observations of crystallographic phase transformations in Cs [Schwarz et al., Phys. Rev. Lett. **81**, 2711 (1998)], CsH [Ghandehari et al., Phys. Rev. Lett. **74**, 2264 (1995)], NaBr and NaI [Leger et al., J.Phys.:Condens. Matter **10**, 4201 (1998)] and Sr [Winzenick and Holzapfel, Phys. Rev. B **53**, 2151 (1996)]. The calculated transition pressures agree with the experimental data. We also predict a similar high pressure behaviour for RbH and KH as observed for CsH but not for NaH and LiH.

X-ray diffraction studies of alkaline and lanthanide metals at high pressure

M.I. McMahon (University of Edinburgh)

These are exciting times in high-pressure research. The advent of x-ray diffraction techniques that allow the routine refinement of atomic coordinates for the first time, coupled with the advances made in ab initio computational techniques, are enabling great advances to be made in our understanding of how materials behave at high pressure. However, these twin advances now make it more important than ever to understand those systems where theory and experiment do NOT agree. We have recently made diffraction studies of the long-uncertain structure of Sr-III (stable between 26 and 35GPa [1]), and the long-disputed structure of Ce-V (stable between 5 and 12GPa [2]). Both systems have subsequently been the subject of ab initio calculations, the results of which are at odds with experiment. In this talk I will review our experimental results, and suggest some possible reasons for the discrepancies observed with theory.

[1] D.R. Allan, R.J. Nelmes, M.I. McMahon, S.A. Belmonte and T. Bovornratanaraks, Rev. High Pressure Sci. Technol. 7, 266 (1998).

[2] M.I. McMahon and R.J. Nelmes, Phys. Rev. Lett. 78, 3884 (1997).

Vibrational Spectroscopy in Metals and Molecular Crystals at High Pressure

Helmut Olijnyk and Andrew P. Jephcoat (University of Oxford)

The effect of pressure on the phonon spectra obtained by Raman spectroscopy is compared for various metals (Mg, Zn, Zr and some lanthanides), which crystallize in the hcp structure at ambient conditions. The pressure response of the observed phonon modes includes normal behaviour (positive pressure shift) (Zn, Mg) as well as anomalies like splitting of degenerate modes (Mg) and a negative pressure shift (Zr, lanthanides). Available theoretical results are compared with the experimental results.

Raman sudies on dilute isotopically mixed crystals of solid nitrogen up to megabar pressures indicate that vibrational coupling increases with pressure and may suggest the onset of bond weakening for molecules located on particular sites. The phase transitions occurring in the higher pressure regime appear to involve an increase in the number of inequivalent sites, with possibly subtle changes in the orientational behaviour of particular molecules in the pressure range 25 to 50 GPa not readily revealed in recent x-ray diffraction studies.

Pressure tuning of Fermi resonance was studied by Raman scattering in the high-pressure phase CO2-III and for some natural abundant isotopic species. The observed changes in the spectral features of the host crystal suggest that pressure strongly weakens FR and the transition from a two-phonon bound state to a two-phonon unbound state takes place in the 2*2 region between 30 and 40 GPa. It appears that the differences in FR of the isotopic species are mainly controlled by the frequency shifts introduced by the different isotopic masses.

Self-Interaction Corrections in the Electronic Structure Theory of Lanthanides

Axel Svane (University of Aarhus, Denmark)

Electronic structure calculations using the ab-initio self-interaction corrected local-spin-density method are described. In this scheme an integral number of electrons may be localized on the rare earth atom, thus mimicking the atomic-like open f-shell. Applications to cerium compounds give a quantitative correct account of the pressure-induced phase transitions. For the rare earth metals the equilibrium volumes and bulk moduli are calculated in good agreement with experimental data. The pressure-induced phase transitions, which involve the f-electron delocalization, are discussed. Finally, we discuss the calculation of energy differences between divalent and trivalent Yb compounds and the behavior of YbS under pressure.

New crystal structures of elemental metals under pressure

K. Syassen(1), U. Schwarz(1), K. Takemura(2), M. Hanfland(3), O. Jepsen(1)

(1) Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, Germany

(2) Natl. Institute for Research in Inorganic Materials, Tsukuba, Japan

(3) European Synchrotron Radiation Facility, F-38043 Grenoble, France

We have very recently solved the long-standing problem of the crystal structure of Cs-V which occurs above 12 GPa on the basis of high-resolution angle-dispersive powder diffraction data measured at the ESRF. The orthorhombic structure has space group Cmca and 16 atoms per conventional cell. Atoms occupy two different Wyckoff positions with coordination numbers of 10 and 11, respectively. The structure type is a new one among elemental solids. However, it is not unique to Cs. The phase Si-VI, which exists intermediate between eight-fold (primitive hexagonal) and twelve-fold (hcp) coordinated phases, is found to be isostructural to Cs-V. This result is surprising in view of the fact that Cs-V is a d-electron metal, wheras Si-VI is an sp-band metal. It motivated us to perform tight-binding band structure calculations, which reveal interesting differences in the chemical bonding of Cs-V and Si-VI. The structural results obtained for Cs and Si suggest that the Cs-V-type structure may be a possible candidate for several as yet unsolved high-pressure structures of other elemental metals. In fact, the phase Rb-VI stable above 48 GPa is found to also have the Cmca structure, and preliminary diffraction patterns of Ge at 135 GPa are at least consistent with this structure.

Ab Initio Simulations of Materials under High Pressure

Dominik Marx (Max–Planck–Institut, Stuttgart, Germany)

Car–Parrinello *ab initio* molecular dynamics simulations offer a new approach to the theoretical investigation of materials, including in particular non–ambient conditions. A short introduction in the traditional technique at the current status of development will be given. Generalizing these ideas to quantum–mechanical nuclei the *ab initio* path integral technique will be introduced (D. Marx and M. Parrinello, Z. Phys. B **95** (1994) 143; J. Chem. Phys. **104** (1996) 4077). Within the Born–Oppenheimer separation of nuclei and electrons the nuclear degrees of freedom are quantized using the path integral formulation of quantum statistical mechanics, whereas the electrons are represented concurrently using density functional electronic structure theory. This technique is well suited to study materials where the quantumness of protons cannot be neglected.

Two recent applications will be discussed: Ice and solid hydrogen at high compression (M. Benoit, D. Marx, and M. Parrinello, Nature **392** (1998) 258; S. Biermann, D. Hohl, and D. Marx, Solid State Commun. **108** (1998) 337). These are two fascinating systems showing pressure–induced phase transitions at conditions that are currently in reach of diamond–anvil–cell experiments. For ice at 100 K it is found that the sequence of phase transitions is antiferroelectric ice VIII to paraelectric (translationally–disordered) ice VII and finally to symmetric ice X at about 100 K. Furthermore, it is found that the antiferroelectric disordering is driven by translational proton tunneling, whereas the symmetrization is due to zero–point motion. These different quantum effects are also the reason for the measured isotope shifts. Finally, two "forms" of ice X both with a unimodal proton distribution centered at the bond midpoint are found: "proton–disordered" and "proton–ordered" symmetric ice at lower and higher pressures, respectively. For solid hydrogen at 50 K in the Megabar regime it is shown that is is insufficient to take into account the effects of zero–point motion in the framework of the (quasi–) harmonic approximation. At very high compression the structure of solid hydrogen is found to be unexpectedly diffuse due to quantum effects.

High pressure crystal structure of methanol and ethanol

Stewart Clark (University of Durham) and David Allan (University of Edinburgh)

For simple molecular systems that interact through short range repulsive forces and attractive weak van der Waals interactions, quantitative interpretation of experimental data can be obtained with models based on effective pairwise potentials. Important classes of intermolecular interactions such as hydrogen bonding, however, escape such modelling. This is exemplified by the existence of many different potential models for water, each one being optimised to a different property. Recently, advances have been made in the description of dense hydrogen bonded systems by ab initio calculations which now allow a systematic study of hydrogen bonding to be made. This is rewarding because competition between various types of interactions causes phase transitions, including glass formation, and affects crystal nucleation. To develop a systematic understanding of hydrogen-bonded molecular systems at high pressure, it is vital that a homologous series of chemical compounds is studied. An important, and prototypic, series of compounds are the linear alcohols H(CH2)nOH, where the integer n denotes the chain length. With increased chain length, it is expected that the effects of hydrogen bonding are reduced. Here, we study the simplest alcohols, with n=1 and 2 and present their high pressure structures and compare them to the known low temperature structures in an attempt to determine any systematic behaviour in hydrogen bonded systems. For methanol, which is the simplest linear alcohol, two orthorhombic crystalline phases are formed on cooling the beta-phase crystallises below 175K and transforms to the alpha-phase at about 157K on further cooling. For ethanol (H(CH2)2OH), only a single crystalline phase, with the monoclinic space group Pc, is observed on cooling below the freezing temperature of approximately 156K at atmospheric pressure. The low-temperature structures of both methanol and ethanol are characterised by infinite hydrogen bonded molecular chains with the molecules arranged in an alternating sequence. In this talk, these structures will also be described in detail.

Structures, disorder, and metastability in ices at medium pressures

John Finney (UCL)

Twenty years ago, little was known about the structures of ice phases at high pressure. Until that time, most structural measurements had been made on samples recovered to ambient pressure at low temperature, and apparent discrepancies between the hydrogen ordering found crystallographically on recovered phases and that implied from dielectric and thermodynamic measurements suggested a need to study the detailed structures under their conditions of stability. Such measurements became possible in the early 1980s on intense neutron sources such as the ILL. This talk discusses some of the more interesting results from studies on ices largely in the complex medium pressure range. In addition to confirming detailed structures, and resolving some uncertainties, aspects of disorder of both oxygens and hydrogens are raised, as well as issues relating to metastable phases. In addition to the recently discovered new ice phase XII, powder patterns have been observed of at least two phases whose structures have yet to be solved. The primary early motivation for this work was to provide high quality structural data for refining models of the water-water hydrogen bond under a range of temperature and pressure conditions. The results so far have confirmed the importance of repulsive restraints in determining orientational structure, and possibly the molecular disorder. Measurements within particular phases as functions of both temperature hand pressure have produced reliable compressibilities and expansivities for further testing of our quantitative understanding of the water-water hydrogen bond.

High-pressure structural studies of ice and ices

John Loveday and Richard Nelmes (University of Edinburgh)

The high-pressure behaviour of the simple molecular ices (H_2O, NH_3, CH_4, H_2S) provides fundamental information on the density dependence of important interatomic interactions such as hydrogen bonding. And, since many ices are important constituents of the outer planets and satellites, their high-density properties also underpin planetary modelling. The structures of high-pressure phases and their structural pressure dependence are the most basic of high-pressure information and vital for the interpretation of all other measurements. In addition, the high-pressure behaviour of ices is one of the current important challenges in ab-initio calculations; accurate structural information provides a valuable cross-check for modelling studies. However, because prior to 1990 neutron diffraction was limited to pressures below 3 GPa (30 kbar), the accuracy of structural information in ices was limited by the need to depend on light-scattering and x-ray diffraction. The development of the Paris-Edinburgh cell has now increased the pressure range for neutron diffraction by a full order of magnitude to ˜30 GPa (300 kbar) and has provided much new, detailed information on the structures of ices at high pressure. Some examples are that the previously unknown structures of the high pressure phases ammonia-IV and deuterium sulphide I' have been solved and shown to be quite different from what had been surmised from light-scattering and x-ray diffraction work. Studies of the structural pressure dependence of ice VIII have shown that the effect of hydrostatic pressure on hydrogen bonds is different from that expected from chemical substitution at ambient pressure. And structural studies of the high-pressure phases of methane and the ammonia hydrates suggest a remarkable and increasing structural complexity at high pressures contrary to the previously held view that the high-pressure structures of ices were in general simple. In the case of ice itself, a detailed comparison of the structures of ices VII and VIII has shown that ice VII has multi-site oxygen disorder importantly different from what had previously been believed. This implies that its hydrogen bond network is quite different from that of ice VIII, and more complex. Measurements to 25 GPa reveal that these differences are pressure-independent, or nearly so, and probably persist up to the transition to ice X – with its centered H-bonds – which has recently be identified in the range 60-100 GPa. Neutron diffraction results are thus starting to have influence on studies of ices in the very high pressure range.

High-pressure behavior of minerals

Martin Dove (University of Cambridge)

High-pressure studies are of crucial importance to the mineral sciences, and indeed some of the major developments in the field of high-pressure experiments have been driven by mineral scientists. In this talk I report on some of the work of our high-pressure work using neutron and synchrotron radiation (particularly the minerals lawsonite and calcite), much of which is concerned with phase transitions. This programme of work is backed up with calculations using empirical models for interatomic interactions. I will also introduce the theoretical methods we use for analysing phase transitions that occur at high temperature and ambient pressure, and note the new features that are required when one considers high-pressure phase transitions.

5.2 Reports on Collaborative Visits

Report on a visit of Robert Kucharczyk (Wrocław, Poland) to Professor Johannes Pollmann's group (Münster, Germany)

November 11 - December 5, 1998

Within the STRUC-Ψ_k ESF Programme, I have spent four weeks (9.11.98–5.12.98) at the University of Münster, in the group of Professor Johannes Pollmann, to start a joint scientific project on *'Electronic properties of superlattices from pseudopotential calculations'*.

During my stay in Münster, I got used to computer codes already developed and used in Professor Pollmann's group for supercell calculations of the electronic structure of various semiconductors within a plain-wave basis set.

These have been adopted to a specific superlattice geometry and applied to the GaAs/AlAs(001) system as a concrete example. As a first step, a modern empirical pseudopotential of Mäder & Zunger [K. Mäder and A. Zunger, Phys. Rev. B **50**, 17393 (1994)] has been implemented to represent the potential of such a superlattice. Within this approach, the electronic structure of GaAs/AlAs(001) superlattices with different thicknesses of the constituting GaAs and AlAs slabs has been computed. In addition to studying the superlattice band structure and its dispersion along high-symmetry lines of the superlattice Brillouin zone, the spatial distribution of particular superlattice states has been examined by means of planar-averaged squared moduli of the corresponding wave functions. In particular, a significant effect of the Γ-X mixing on the energy level structure in the conduction band range (neglected within an effective-mass approximation) and the related type-I/type-II superlattice transition have been noticed.

The above method has also been applied to investigate the electronic structure of the so-called polytype (or: complex-basis) superlattices, whose period consists of more than two different semiconductor slabs. Preliminary results for asymmetric-double-well, as well as, asymmetric-double-barrier bases have been obtained. These are the systems of my particular current interest, which I have treated previously only within the modellistic effetive-mass approaches.

In summary, my stay in Münster with the group of Professor Pollmann enabled me to start more realistic electronic structure calculations of semiconductor superlattices, which I am going to continue upon return to Wrocław and which we plan—in a close collaboration with Professor Pollmann's group—to further extend by adopting selfconsistent approaches and using *ab-initio* pseudopotentials.

Robert Kucharczyk

Münster, December 5, 1998.

Report on the collaborative visit of K. Kádas (TU Budapest) to Professor Jürgen Hafner's group (TU Wien, CMS Wien)

16 November - 11 December 1998

As a postdoc fellow at the Technical University of Budapest I work on the theoretical investigation of solid surfaces and amorphous systems. I visited the group of Professor Jürgen Hafner at the TU Wien from 16 November to 11 December 1998. We have already started a collaborative work on the reconstruction of low index surfaces of cubic BN earlier and summarized the first results in a paper (K. Kádas, G. Kern and J. Hafner: Ab initio studies of the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of cubic BN; Phys. Rev. B, in press). We continued our collaboration during my visit to Vienna by the detailed investigation of the electronic and band structure of cubic BN surfaces for the surface reconstruction models have been found stable previously. We applied the VASP (Vienna Ab-initio Simulation Package) local-density-functional code developed in Professor Hafner's group.

Krisztina Kádas

Budapest, 14 December 1998

Report on a visit of A. Lichtenstein (Jülich) to Karel Kunc (University Pierre and Marie Curie, Paris VI)
July, 1998

During the short visit (one week in July 1998) we established a general program of work aimed to apply the LSDA+U scheme and dynamical-mean field theory (DMFT) to the investigation of the electronic structure and optical properties of magnetic oxides, the CMR-manganites, as well as classical Mott-Hubbard oxide, like VO_2. This problem is strongly linked to the project currently pursued by experimental group in the University Pierre and Marie Curie. Investigations of the optical properties of such correlated systems is a hard problem for electronic structure theory. Analyses of the experimental data, shows that optical spectra could change drastically during Metal-insulator transition as functions of small doping or temperature. This affects the electronic states not only in the small energy region near the Fermi energy, but also on a large energy scale of the order of 2-3 eV. In order to reproduce such a big change in the electronic structure calculations, one need to take into account the formations of additional correlated states, such as satellites and the Hubbard bands. We discuss a possibility of calculations a such type of effects in general LDA+U scheme including the self-energy contributions in the DMFT approximation.

The problem of accurate calculations of the total energy and crystal distortions for correlated electronic materials was also discussed. The structural-distortion effects are very important for careful description of electronic structure of the CMR-manganites. We will try different full-potential codes to find the best one for the electronic structure of correlated magnetic oxides. We discuss some experience of the leading computational groups in the LDA+U total energy calculations within the LMTO, LAPW and pseudopotential methods. We expect to have few publications on this project.

A. Lichtenstein

6 General Workshop/Conference Announcements

6.1 XMCD Meeting

XMCD Specialist Users' Meeting
Daresbury Laboratory, Warrington, UK
Monday 17th May 1999

A general meeting on the science, instrumentation, experiments and theory of X-ray Magnetic Circular Dichroism (XMCD). This one-day meeting is of interest for research groups in university and industry working in the field of magnetism and magneto-optics.

Invited speakers:

J. A. D. Matthew, *York*	Opening and introduction to XMCD
G. van der Laan, *DL & York*	Dichroic photoemission & related phenomena
E. Dudzik, *York & DL*	Instrumental developments at the SRS
J. A. C. Bland, *Cambridge*	Spin-valve materials
G. Short, *York*	Transverse XMCD
C. Binns, *Leicester*	Fe clusters
S. S. Dhesi, *DL*	3D magnetometry of orbital moments
R. A. D. Pattrick, *Manchester*	XMCD in Earth Science
W. Schwarzacher, *Bristol*	Transmission of thin Co films
K. Fleury-Frenette, *Liege*	Dy-Fe and Dy-FeCo magneto-optical alloys
A. C. Jenkins, *DL & Munich*	Magnetic EXAFS calculations on Gd

Poster session; Sponsored buffet lunch in the Science Centre; Science exhibition; Optional tour of the Magnetic Spectroscopy Lab and the Synchrotron.

There is no registration fee. Posters are welcome.
Advance notice of participation is recommended.

For more information: Esther Dudzik (e.dudzik@dl.ac.uk)
http://www.dl.ac.uk/SRS/

6.2 ChiPPS 2000 Workshop

ChiPPS 2000, Germany
International Workshop on Challenges in Predictive Process Simulation

ab-initio:physics:technology:modeling:diffusion:deposition:etch

ChiPPS is designed as a “call for action” interdisciplinary summer school. It brings together experts in basic materials science, in the processing of microelectronic devices, and in the development of simulation tools. It is meant to stimulate research by clarifying how the needs of microchip technologies match our knowledge of critical fundamental processes. We build a bridge between those who study physics at the atomic scale and those who simulate technological steps to make money. Attention is paid to the potential role of parameter free (ab initio) calculations as a source of unbiased physical information. Visit http://www.ihp-ffo.de/chipps.html to find out more about us.

The first ChiPPS took place in August 1997 in Wandlitz near Berlin, Germany. It was devoted mostly to technological problems related with diffusion of dopants in silicon. This three-day meeting gathered about 80 persons from 10 countries and was very positively evaluated by the participants.

The next ChiPPS will be organized in the year 2000 in Germany. The tentative date is April. The focus will be on technological problems related with interconnecting devices on a chip (back end processes). As in the previous meeting, these issues will be presented in the context of the whole technological process, the most promising goals for basic research will be sorted out, and methods to achieve them will be discussed.

To receive current information about the status of the ChiPPS project, please fill the (not binding) pre-registration form:

PLEASE RETURN TO: chipps@ihp-ffo.de

(...) I would consider participation in April 2000
(...) I would consider participation, but April is not good
(...) I would consider submitting an abstract

(...) Please keep me informed about ChiPPS
(...) I have never heard about ChiPPS
(...) Please remove my name from the mailing list

Please visit: **http://www.ihp-ffo.de/chipps.html** to learn about ChiPPS. TEL: +49(335) 5625-316, FAX: +49(335) 5625-300, E-mail: chipps@ihp-ffo.de.

7 General Job Announcements

URGENT ANNOUNCEMENT: POST-DOCTORAL POSITION

Departamento Fisica Teorica, Atomica y Molecular, Universidad de Valladolid, Valladolid, SPAIN

Candidates are invited to apply for post-doctoral position(*) to work on the electronic, structural and transport properties of carbon and composite-nanotubes. Particular emphases are on the nanoestructures theory: STM microsopy, nanodevices, chemical activity, mechanical behavior, optical response. In addition, the group is flexible and open to promising new research directions. The techniques to be used range from empirical potentials to acurate ab-initio methods. Knowledge of molecular dynamics and electronic structure calculations is desired. The position is already available and is for two years. Further information on the research of the group as well as publication list can be found in my web page:
`http://www.fam.cie.uva.es/~arubio`.

The project is included in an EU-funded Training and Mobility Research (TMR) Network on "Nanotubes for Microstructure Technology" (NAMITECH). A very close collaboration between the experimental partners of the network and the theoretical group is expected. Please see the web page of the Network for further details
(`http://www.gdpc.univ-montp2.fr:7082/~henrard/Namitech`) including a monthly published Newsletter.

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. Accepted formats are paper, ascii/LaTeX/postscript/pdf email attachment, or a web address for html, LaTeX, ps, or pdf versions of the above. xxx or PR-online links are ok for the publication. Web links are the preferred format for all materials.

Applications should be sent to:

Dr. Angel Rubio
Departamento Fisica Teorica
Universidad de Valladolid
E-47011 Valladolid. SPAIN

Phone : ++34-983-423263
Fax : ++34-983-423013
E-mail: arubio@mileto.fam.cie.uva.es
`http://www.fam.cie.uva.es/~arubio`

(*) 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. Only nationals of Member States or Associated States of the EU (but not Spain) are eligible for the position allocated to the Valladolid node.

Postdoctoral Position in Solid State Theory Group

National Renewable Energy Laboratory

http://www.sst.nrel.gov

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for a postdoctoral research position to start in the summer or fall of 1999. Applications are accepted now. The position is for two years, renewable upon mutual agreement to a third year, and is in the area of development of electronic structure theory, algorithms and applications to nanostructures and alloys. The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists at NREL. The group has outstanding computational facilities, an excellent basic-research atmosphere, and is located near the beautiful Rocky Mountains. For more information about the group research activities, publications and personel, see http://www.sst.nrel.gov. Interested candidates should immediately send in writing (no e-mail submission) a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and should arrange for 2-3 reference letters to be sent directly to:

Dr. Alex Zunger
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado, 80401

NREL is an equal opportunity/affirmative action employer.

Postdoctoral Position in Electronic Structure
Austin, Texas

Postdoctoral position is available in electronic structure calculations starting May 1, 1999. Applicants must have obtained Ph.D. in the past 3 years and be available for reappointment for a second year. Salary $25,000/year plus fringe benefits. Because of health insurance costs, applicants without dependants preferred. Send applications to **Prof. L. Kleinman, Department of Physics, University of Texas, Austin, Texas 78712 or email to kleinman@mail.utexas.edu.**

Postdoctoral Position at CECAM
CECAM, Lyons, France

CECAM (Centre Europeen de Calcul Atomique et Moleculaire) is a European Center located in Lyons at the Ecole Normale Superieure. It is dedicated to the development of simulation techniques in Condensed Matter, Atomic and Molecular Physics. The activities of CECAM consist in the organization of workshops, doctoral, postdoctoral and sabbatical stays dedicated to research projetcs elaborated at the level of an European cooperation. Within this framework, an opening for a postdoctoral stay for one year in 1999, is hereby advertized. This position is part of a cooperation involving CECAM, the Commisariat à l'Energie Atomique (CEA-France) and the Ecole Normale Superieure de Lyon.

Applications are invited for a postdoctoral research position in Non-Equilibrium Molecular Dynamics within the project

" Microscopic modelling of solids under shock "

The study to perform will consist of the following parts:

1. development of NEMD codes for large numbers of particles on parallel computers
2. development of these techniques for the case of a shock in solids
3. study of the kinetics of melting transition after the shock.

The simulation results will, in the future, lead to confrontation with experimental data and to the modelling of the after-shock fragmentation.

Applicants should preferably have good knowledge of Statistical Mechanics and Solid-State Mechanics and a substantial experience in Molecular Dynamics simulation techniques.

Remuneration and conditions of employment

The successful applicant will have a one-year contract at CECAM with a salary fixed by the CNRS scale: the Charge de Recherche CNRS scale ranges from 11 400 FF to 16 900 FF net per month, according to experience. The position is available starting early 99. Further information can be obtained from Professor Michel Mareschal (Michel.Mareschal@cecam.fr; tel: +33-4 72 72 86 38, fax 8636, secr. 8637).

Submission

Candidates should send their CV and list of publications with a letter of motivation to:

Professor M. Mareschal
CECAM
ENS-LYON
46, allee d'Italie
69364 LYON cedex 7
FRANCE
web: www.cecam.fr

Postdoctoral Fellow in Computational Nanoscience

National University of Singapore

http://www.cz3.nus.edu.sg/

A postdoctoral research fellow is available at the Department of Computational Science, National University of Singapore. The applicant is expected to have a strong background in ab initio first-principles computation and demonstrated expertise in large-scale computation and programming. The successful applicant will be hired under the computational nanoscience programme, which is a new multi-disciplinary initiative focusing on computational approach to study nano-scale devices and their structural, electronic, magnetic, and transport properties. The computational nanoscience programme is very well-equipped with the state-of-art workstations with access to a number of supercomputers. The computational nanoscience group also has strong international collaborations with many leading theoretical and experimental groups.

The initial offer will be for one year, which can be extended for another year subject to performance. The gross salary is at Singapore dollar $60,000 per annum (US$1 = S$1.65).

The applicants should submit a curriculum vitae, a list of publications, two most important recent papers, and suggested three names and addresses (postal, email, and fax) of individuals as potential references to:

Assoc. Prof. Jian-Sheng Wang,
Department of Computational Science,
S17 Level 7,
National University of Singapore,
Singapore 119260

The deadline is 31 March 1999. For more information, visit our web site http://www.cz3.nus.edu.sg/.

Postdoctoral Research Assistant

Department of Physics and Astronomy and Chemistry, Queen's University, Belfast, UK

RA1A £15,537 - £23,651

http://www.cz3.nus.edu.sg/

A post-doctoral position is available for up to 24 months to work on an EPSRC funded project, "The use of XANES and ELNES for the characterisation of stabilised zirconia". The project is a collaboration between Glasgow University, The Queen's University, Belfast, MEL Chemicals Ltd and Johnson Matthey Ltd. The part of the project associated with this post involves modelling the near edge fine structure present on the edges observed in x-ray absorption spectroscopy and electron energy loss spectroscopy. Experience with first principles band structure calculations is essential and a background in the theoretical interpretation of spectroscopic techniques such as ELNES and XANES would be highly desirable, as would a knowledge of many-body physics. The post will be based in Glasgow but will involve extended periods at The Queen's University working with Professor Finnis and the Atomic Simulations Group.

Further information is available at http://www.ssp.gla.ac.uk/ or from Professor Alan Craven, Department of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ. (Tel: 0141 330 5892, FAX: 0141 330 4464, E-mail: a.craven@physics.gla.ac.uk) to whom applications, including a CV and the names of two referees, should be sent.

Post-doctoral Position in Condensed Matter Theory

University of Uppsala, Sweden

One or two post-doctoral positions are available in the area of electronic structure theory of solids from January 1999. The positions are available for one year and may be extended for one more year. The main aim of the project is to perform atomistic simulations of technologically important systems such as hard materials, ductile materials, Solar energy materials, and magneto-optic materials. First principles calculations, based on density functional theory (in combination with accurate total energy methods: FPLMTO and FPLAPW) and molecular dynamics simulation, will be used.

Applicants should have, or expect soon to obtain, a PhD in Physics or Chemistry, with experience in computational condensed matter theory. Interested persons should send their resumes and the names of references as soon as possible.

Dr. O. Eriksson, olle.eriksoon@fysik.uu.se, Tel: +46 18 471 3625
Dr. R. Ahuja, rajeev.ahuja@fysik.uu.se, Tel: +46 18 471 3626

Department of Physics,
University of Uppsala,
Box 530
751 21 Uppsala, SWEDEN
FAX: +46 18 471 3524

POSTDOCTORAL POSITION IN CONDENSED MATTER THEORY AT THE UNIVERSITE CATHOLIQUE DE LOUVAIN, LOUVAIN-LA-NEUVE, BELGIUM

One postdoctoral position in the Condensed Matter Theory group at the Department of Materials Science is becoming available, beginning between August and October 1999.

The research activity will include studying materials at the atomic scale using a density-functional theory plane-wave code (and making eventual improvements to this code). As this position is funded by a Interuniversity Attraction Poles program of the federal state, the systems to be studied should be chosen among those also investigated by experimentalist groups in this program, including semiconductor heterostructures, oxyde interfaces, carbon-based materials, magnetic multilayers ... .

The appointment is one year, renewable depending upon the availability of funds. The candidate should have a good experience in ab-initio calculations using density-functional theory and in code development.

Interested persons should send their resumes, with two letters of recommendations, to:

Dr. Xavier Gonze
Unite de Physico-Chimie et Physique des Materiaux
Place Croix du Sud, 1
B-1348 Louvain-la-Neuve
BELGIUM
email: gonze@pcpm.ucl.ac.be

See the URL http://www.mapr.ucl.ac.be/Fr/PCPM/abinit.html for a description of the research group, http://www.mapr.ucl.ac.be/Fr/PCPM for a description of the laboratory, `http://www.fundp.ac.be/~ph` for a description of the Interuniversity Attraction Pole program on reduced dimensionality systems.

POSTDOCTORAL OPPORTUNITIES IN MATERIALS THEORY

Pennsylvania State University Department of Physics

The Crespi group at the Pennsylvania State University Department of Physics will have 2 or 3 postdoctoral openings available in Materials Theory starting any time in the next 1-12 months. Particular emphases are the theory of carbon nanostrucures (e.g. adsorption, electronic devices, novel composites, etc.), development of new many-body interatomic potentials using maximum entropy techniques, global structural optimization, and applications of density functional theory in collaboration with experiment. In addition, the group is flexible and open to promising new research directions within Materials Theory.

The group is funded by a combination of the David and Lucile Packard Foundation Fellowship, the National Science Foundation CAREER Award, the Research Corporation Research Innovation Award, and the Petroleum Research Foundation. Depending on circumstances, one or more of these positions might be convertible into an ongoing (non-tenure track) research assistant professorship position.

Resources available to the Crespi Group include a cluster of Alpha workstations, NPACI supercomputer allocations, and 1500 square feet of (soon-to-be) renovated office space (shared with J. Jain). The Pennsylvania State University's internationally recognized materials research effort encompassses over 170 faculty in the interdisciplinary Materials Research Institute and provides numerous opportunities for fruitful collaboration both within theory and between theory and experiment.

Applications should include a CV and one selected publication. Accepted formats are paper, ascii/LaTeX/postscript/pdf email attachment, or a web address for html, LaTeX, ps, or pdf versions of the above. xxx or PR-online links are ok for the publication. Web links are the preferred format for all materials. Microsoft Word electronic documents will not be accepted.

Please send applications to:

Professor Vincent H. Crespi
Center for Materials Physics
104 Davey Laboratory
University Park, PA 16802-6300

or via email to: vhc2@psu.edu. The group's research webpage is available at: `http://www.phys.psu.edu/~crespi`. Please forward this information to interested parties via email, or by posting the attached postcript and pdf versions of this notice. These files are also available from the website listed above.

Post-doctoral Position
Electron Spectroscopic Studies of Fullerene-based Materials

University of Uppsala, Sweden

Within the newly-started EU-TMR Programme FULPROP a postdoctoral position in Electron and X-ray Spectroscopy Studies of Fullerene-based Materials (duration 12 - 36 months) is to be filled in the Department of Physics at Uppsala University, available immediately. Applicants should have some background in Physics or Chemistry, and surface science experience is quite helpful.

The position offers opportunities for close collaboration with groups in Austria, Belgium, France, Germany, Italy, the Netherlands, the U.K., and Switzerland. Applicants should fullfill TMR requirements: non-Swedish European (and associated country–Iceland, Israel, Liechtenstein, and Norway) citizens under 35 years of age.

We plan to compare bulk to surface electronic structure of fullerene compounds and of endohedral fullerenes, and to try to understand the implications on electronic and materials properties of the unique physical structure (e.g., metal in carbon cage). The experimental techniques to be used and/or learned include Photoelectron Spectroscopy (PES and XPS), X-ray Absorption and Emission (XAS and XES).

Applications should include a curriculum vitae, list of publications, description of scientific interests, and names and addresses of two or three references.

Deadline: open until position is filled.

Please contact:

Paul Bruhwiler,
Dept. of Physics, Uppsala University
Box 530
SE-751 21 Uppsala
Sweden

+46 70-425 0057 (mobil, answering machine)
+46 18-471 3613 (office)
+46 18-471 3524 (fax)
Mailto:Paul.Bruhwiler@fysik.uu.se.

8 Abstracts

Magnetic circular dichroism in Tb $3d \to 4f$ resonant photoemission

G. van der Laan
Daresbury Laboratory, Warrington WA4 4AD, United Kingdom
E. Arenholz, Z. Hu, A. Bauer, E. Weschke, Ch. Schüssler-Langeheine,
E. Navas, A. Mühlig, G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin,
D-14195 Berlin-Dahlem, Germany
J. B. Goedkoop and N. B. Brookes
European Synchrotron Radiation Facility, BP 220,
F-38043 Grenoble, France

Abstract

We present an elegant method to calculate the magnetic circular dichroism in the resonant photoemission decay of lanthanides. By recoupling the angular momenta we obtain fundamental spectra which require only the reduced matrix elements. The full multiplet calculations in intermediate coupling using the t-matrix approach are compared to new experimental results for the Tb $3d \to 4f$ resonant photoemission taken at high-energy resolution. The agreement for the $M_{4,5}$ absorption structures as well as for the $4f$ photoemission is remarkably good. Angular momentum coupling plays an important role in the magnetic circular dichroism (MCD). As a rule we find that a strong negative ^8S peak in the resonant photoemission MCD is indicative for a dominantly $J' = 7$ character in the intermediate x-ray absorption state while a strong positive ^6I peak indicates a dominantly $J' = 5$ character. The photoemission signal observed for the ^6H and ^6G final states is reduced compared to the calculation, which might be due to configuration interaction with other shells, such as the $5p$ and $5d$. At higher photon energies within the $M_{4,5}$ absorption, an enhanced photoemission is found at binding energies above 12 eV, which can be ascribed to "spin-flip" transitions.

(Submitted to Phys. Rev. B)
Manuscripts available from: g.vanderlaan@dl.ac.uk

Orbital polarization in $NiFe_2O_4$ measured by Ni 2p x-ray magnetic circular dichroism

Gerrit van der Laan[1,2], C.M.B. Henderson[1,3], R.A.D. Pattrick[1,3], S.S. Dhesi[1,2],
P.F. Schofield[4], E. Dudzik[1,2], and D.J. Vaughan[3]
[1] *Daresbury Laboratory, Warrington WA4 4AD, UK*
[2] *Department of Physics, University of York, York YO1 5DD, UK*
[3] *Department of Earth Science, University of Manchester,*
Manchester M13 9PL, UK
[4] *Department of Mineralogy, Natural History Museum,*
London SW7 5BD, UK

Abstract

We report a comprehensive study of the x-ray magnetic circular dichroism (XMCD) at the Ni $L_{2,3}$ edges of $NiFe_2O_4$ (trevorite), a ferrimagnetic compound which belongs to the class of strongly correlated $3d$ systems. The measured XMCD line shape is in good agreement with full-multiplet calculations for a $3d^8$ ground state including an octahedral crystal field of $10Dq = 1.2$ eV. Using the XMCD sum rules we find for the nickel an orbital to spin magnetic moment ratio of $L/S = 0.27 \pm 0.07$, which means that the orbital contribution to the magnetic moment is $12 \pm 2\%$. The size of the error bar is not due to the neglect of band structure and hybridization, but due to Coster-Kronig transitions which give a transfer of spectral weight in the dichroism near the L_2 edge. Using the sum rules for the isotropic x-ray absorption spectrum we obtain the expectation value of the spin-orbit interaction, which can be converted into an L/S ratio of 0.34 ± 0.11. All sum-rule results were corrected for the influence of core-valence exchange interaction, which gives rise to jj mixing between the two absorption edges. The correction is done by comparing the calculated sum rule results with the correct ground state values calculated as a function of crystal field strength. The 2-eV shoulder of the L_3 line shows a strong positive dichroism, which can be attributed to a spin-flip state. From the overall agreement between the experimental and theoretical results we conclude that a localized model provides a good description for the orbital magnetization.

(Phys. Rev. B, accepted)
Manuscripts available from: g.vanderlaan@dl.ac.uk

Magnetic linear x-ray dichroism as a probe of the magnetocrystalline anisotropy

Gerrit van der Laan
Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

Abstract

We show that for itinerant $3d$ transition metal systems the magnetocrystalline anisotropy energy is directly related to the anisotropic part of the spin-orbit interaction, rather than to the orbital part of the magnetic moment as was previously suggested. We further show how the spin-orbit anisotropy can be obtained by applying the sum rule for magnetic linear dichroism in x-ray absorption. This provides an element specific tool to study metallic multilayer systems displaying novel magnetic properties, such as perpendicular magnetic anisotropy.

(Phys. Rev. Letters, accepted)
Manuscripts available from: g.vanderlaan@dl.ac.uk

Cobalt impurities on noble metal surfaces

Mariana Weissmann$^+$, Andrés Saúl*, Ana Maria Llois$^+$, and Javier Guevara$^+$
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Avenida del Libertador 8250, 1429 Buenos Aires, Argentina
**Centre de Recherche sur les Méchanismes de la Croissance Cristalline, CNRS,*
Campus de Luminy, Case 913, 13288 Marseille Cedex 9, FRANCE

Abstract

First principles calculations, based on the local spin density approximation, are performed for cobalt atoms deposited on noble metal surfaces. The local density of states at the cobalt site shows a narrow peak at the Fermi energy, which is of minority spin and d character. The d orbital of $m = 0$ symmetry, which must be mostly responsible for tunneling conductance from this surface site, makes a substantial contribution at E_f. Due to hybridization the same peak also appears, but reduced, at neighbor atoms. This result can be used for the interpretation of recent cryogenic scanning tunneling microscopy experiments.

(Phys. Rev. **B59**, (1 April 1999))
Manuscripts available from: weissman@cnea.edu.ar

Tight-binding study of CO chemisorption effect on cobalt magnetization

Štěpán Pick [1] and Hugues Dreyssé [2]
[1] *Jaroslav Heyrovský Institute of Physical Chemistry,*
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CZ-182 23 Prague 8, Czech Republic
[2] *Institut de Physique et Chimie des Matériaux de Strasbourg,*
UMR CNRS 46, 23 rue du Loess, BP 20 CR,
F-67037 Strasbourg Cedex, France

Abstract

By using a semiempirical self-consistent tight-binding scheme we study the effect of O and CO chemisorption on the Co(0001) surface magnetization. Similar calculations are performed for the Co_{12} and Co_{55} clusters of high symmetry. The CO molecule in the atop position, but not in the bridge geometry, is effective in a local magnetization quenching. In clusters, magnetic phase transitions are observed as the Co-CO separation varies. When the separation is more than about 1.8 $\AA$, the Co magnetization remains strong. The character of phase transitions conforms to the formal predictions based on the Landau theory.

(To appear in Phys. Rev. B (Feb. 1999))
Manuscripts available from: hugues@Taranis.u-strasbg.fr

First principles calculations of the ideal cleavage energy of bulk niobium(111)/α-alumina(0001) interfaces

I. G. Batirev, A. Alavi and M. W. Finnis
Atomistic Simulation Group, School of Mathematics and Physics,
The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland, UK
T. Deutsch
CEA, SP2M, CENG, 17 rue des Martyrs, 38054, Grenoble Cedex 9, France

Abstract

We report *ab initio* calculations of the work of adhesion for O- and Al-terminated Nb(111)/α-alumina(0001) interfaces. Strong ionic bonds formed by Nb4d → O2p electron donation account for the high adhesive strength of O-terminated interfaces. However, cleavage preferentially occurs between metal atoms at both O- and Al-terminated interfaces, and their adhesion has both covalent and ionic character.

(Phys. Rev. Lett. (February, 1999))
Manuscripts available from: m.finnis@qub.ac.uk

Universality of the Hohenberg-Kohn functional

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

Abstract

A comment is made on the exchange-correlation potential for two-particle systems with the harmonic interaction $u(x_1, x_2) = k(x_1 - x_2)^2/2$ presented by H. L. Neal in Am. J. Phys. **66**, 512 (1998). We point out that the underlying Hohenberg-Kohn functional is not in general exact, as claimed by the author, but really constitutes an approximation in the same spirit as the local-density approximation.

(Submitted to Am. J. Phys. (October 1998).)
Contact person: schindlmayr@fhi-berlin.mpg.de

Theory of point defects in GaN, AlN and BN: Relaxation and pressure effects

I. Gorczyca, *High Pressure Research Center PAN, Sokolowska 29,*
01-142 Warsaw, Poland
A. Svane and N. E. Christensen
Institute of Physics and Astronomy, University of Aarhus,
DK-8000 Aarhus C, Denmark,

Abstract

Native defects and some common dopants in cubic GaN, AlN and BN are examined by means of *ab initio* calculations using a supercell approach in connection with the full-potential linear muffin-tin-orbital method. The atomic positions, the electronic structure and the defect formation energies are calculated. In particular the vacancies are calculated to be abundant defects. The high pressure behavior of the defect states is also studied and it is found that the pressure coefficients of the defect states depend mainly on their position in the energy gap.

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

A model for Nucleation in GaAs Homoepitaxy derived from First Principles

Peter Kratzer, Caroline G. Morgan*, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany
**Permanent adress: Wayne State University, Detroit, MI, USA*

Abstract

The initial steps of MBE growth of GaAs on $\beta2$-reconstructed GaAs(001) are investigated by performing total energy and electronic structure calculations using density functional theory and a repeated slab model of the surface. We study the interaction and clustering of adsorbed Ga atoms and the adsorption of As_2 molecules onto Ga atom clusters adsorbed on the surface.The stable nuclei consist of bound pairs of Ga adatoms, which originate either from dimerization or from an indirect interaction mediated through the substrate reconstruction. As_2 adsorption is found to be strongly exothermic on sites with a square array of four Ga dangling bonds. Comparing two scenarios where the first As_2 incorporation occurs in the incomplete surface layer, or alternatively in a new added layer, we find the first scenario to be preferable. In summary, the calculations suggest that nucleation of a new atomic layer is most likely on top of those surface regions where a partial filling of trenches in the surface has occurred before.

(Submitted to Phys. Rev. B (December, 1998))
Contact person: kratzer@fhi-berlin.mpg.de

Improving the Efficiency of FP-LAPW Calculations

Max Petersen[1], Frank Wagner[1], Lars Hufnagel[1], Matthias Scheffler[1],
Peter Blaha[2], and Karlheinz Schwarz[2]
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Abstract

The *full-potential linearized augmented-plane wave* (FP-LAPW) method is well known to enable most accurate calculations of the electronic structure and magnetic properties of crystals and surfaces. The implementation of atomic forces has greatly increased its applicability, but it is still generally believed that FP-LAPW calculations require substantial higher computational effort compared to the pseudopotential plane wave (PPW) based methods.

In the present paper we analyse the FP-LAPW method from a computational point of view. Starting from an existing implementation (WIEN95 code), we identified the time consuming parts and show how some of them can be formulated more efficiently. In this context also the hardware architecture plays a crucial role. The remaining computational effort is mainly determined by the setup and diagonalization of the Hamiltonian matrix. For the latter, two different iterative schemes are compared. The speed-up gained by these optimizations is compared to the runtime of the "original" version of the code, and the PPW approach. We expect that the strategies described here, can also be used to speed up other computer codes, where similar tasks must be performed.

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LDA++ approach to electronic structure of magnets: correlation effects in iron

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Abstract

A novel approach to investigation of correlation effects in the electronic structure of magnetic crystals which takes into account a frequency dependence of the self energy (so called "LDA++ approach") is developed. The fluctuation exchange approximation is generalized to the spin-polarized multi-band case and its local version is proposed. As an example, we calculate the electronic quasiparticle spectrum of ferromagnetic iron. It is shown that the Fermi liquid description of the bands near the Fermi level is reasonable, while the quasiparticle states beyond approximately 1 eV range are strongly damped, in agreement with photoemission data. The result of the spin-polarized thermoemission experiment is explained satisfactory. The problem of satellite structure is discussed.

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Polymorphism in silica studied in the local-density and generalized-gradient approximations

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Abstract

The crystal structures of a large number of silica polytypes (α- and β-quartz, α- and β-cristobalite, β-tridymite, keatite, coesite and stishovite) have been studied using density-functional theory, both in the local-density approximation and including generalized gradient corrections to the exchange-correlation functional. All crystal structures have been optimized by minimizing the total energy with respect to all lattice parameters and to the atomic coordinates within the unit cell (up to 40 structural parameters in the case of coesite). The $\alpha \rightarrow \beta$ transitions in quartz and cristobalite have been studied in detail, including different variants proposed for the structure of β-cristobalite. The tetragonal ($I\bar{4}2d$) and simple cubic ($P2_13$) structures are found to be energetically almost degenerate near the equilibrium volume. On volume expansion both structures converge towards the idealized highly symmetric Fd3m structure. A similar continuous transition from a more compact orthorhombic ($C222_1$) to a highly symmetric hexagonal ($P6_3/mmc$) variant is also proposed for β-tridymite. For coesite two monoclinic variants (with C2/c and P2_1/c1 space-group symmetries, respectively) have been examined and found to be energetically degenerate to within 1meV per SiO_2 unit. It is shown that within the local density approximation (LDA) the equilibrium atomic volume of all polytypes is predicted with an accuracy better than one percent. The LDA also leads to excellent structural predictions and to accurate values of the bulk modulus. Corrections in the framework of the generalized gradient approximation (GGA) lead to substantially larger equilibrium volumes, although at fixed volume LDA and GGA lead to identical crystal structures, the increased volume also leads to less accurate structural parameters. However, we find that gradient corrections are essential for achieving accurate structural energy differences between the tetrahedrally coordinated phases found at larger atomic volumes (all polytypes except stishovite) and the octahedrally coordinated high-pressure polymorphs (stishovite and post-stishovite phases).

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Density Functional Study of the Structural and Electronic Properties of $RuS_2(111)$:
I. Bare Surfaces

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Abstract

Electronic and surface relaxation trends as a function of the surface sulfur coverage of $RuS_2(111)$ have been investigated by *ab-initio* density functional calculations. Consistent with experimental and previous theoretical studies, sulfur enriched terminations without exposed unsaturated metal atoms (anionic vacancies) turn out to be more stable compared to the stoichiometric and highly reduced surfaces. Terminations involving the simultaneous occurrence of a full S_2-pair and a single S-atom at the surface are not energetically favored, as predicted by the calculated formation enthalpies and previous Hartree-Fock periodic calculations. The observed S-Ru bond strengthening at the surface for terminations with anionic vacancies is related to the increased hybridization between sulfur 3p-π and ruthenium 4d bands.

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Matrix Methods[1]

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ABSTRACT

We consider techniques for the solution of linear systems and eigenvalue problems. We are concerned with large-scale applications where the matrix will be large and sparse.
We discuss both direct and iterative techniques for the solution of sparse equations, contrasting their strengths and weaknesses and emphasizing that combinations of both are necessary in the arsenal of the applications scientist.
We briefly review matrix diagonalization techniques for large-scale problems.

Keywords: sparse matrices, sparse linear equations, direct methods, iterative methods, large-scale applications, matrix diagonalization, eigenproblems, mathematical software.

AMS(MOS) subject classifications: 65F05, 65F50.

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Current reports available by anonymous ftp from ftp.numerical.rl.ac.uk in the directory "pub/reports". This report is in file duffRAL98076.ps.gz.

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9.1 Introduction

The intention of this paper is to describe current matrix methods for large-scale problems to an audience of computational physicists and chemists. We will discuss both the solution of the linear equations

$$\mathbf{Ax} = \mathbf{b}, \tag{9.1}$$

and the solution of the eigensystem

$$\mathbf{Ax} = \lambda\mathbf{Bx}, \tag{9.2}$$

where the matrices **A** and **B** are large and sparse. The problem (9.2) is called the generalized eigenproblem. The particular, commonly occurring, case where $\mathbf{B} = \mathbf{I}$, viz.

$$\mathbf{Ax} = \lambda\mathbf{x}, \tag{9.3}$$

is called the eigenproblem, or *standard* eigenproblem. The solution of the eigenproblem for all values of λ and $\mathbf{x}$ corresponds to finding a similarity transformation for diagonalizing the matrix and is often called *matrix diagonalization.* In many cases, however, the full diagonal is not required and only a few eigenvalues λ are needed.

Although it is possible to use the solution of the eigenproblem to facilitate solutions of the linear system (9.1), and I have known people to use this route, I should stress that the problem (9.3) is usually much more complicated to solve than the problem (9.1), not least because (9.3) is nonlinear in the unknowns λ and $\mathbf{x}$. Thus, if the solution to (9.1) is all that is required (even for several right-hand sides **b**), then this should be tackled directly.

Sparse systems arise in very many application areas. We list just a few such areas in Table 9.1.

Table 9.1: **A list of some application areas for sparse matrices**

acoustic scattering	4	demography	3	network flow	1
air traffic control	1	economics	11	numerical analysis	4
astrophysics	2	electric power	18	oceanography	4
biochemical	2	electrical engineering	1	petroleum engineering	19
chemical engineering	16	finite elements	50	reactor modeling	3
chemical kinetics	14	fluid flow	6	statistics	1
circuit physics	1	laser optics	1	structural engineering	95
computer simulation	7	linear programming	16	survey data	11

This table, reproduced from [1], shows the number of matrices from each discipline present in the Harwell-Boeing Sparse Matrix Collection. This standard set of test problems is currently being upgraded to a new Collection called the Rutherford-Boeing Sparse Matrix Collection [2] that will include far larger systems and matrices from an even wider range of disciplines. This new Collection will be available from `netlib` (`http://www.netlib.org`) and the Matrix Market (`http://math.nist.gov/MatrixMarket`).

The definition of a large sparse matrix is a matter for some debate. Suffice it to say that we regard a matrix as large if it cannot be factorized efficiently using a code for general linear systems from a standard package for dense systems, such as LAPACK [3]. The order of a matrix that is considered large is thus a function of time depending on the development of both dense and sparse codes and advances in computer architecture. Partly for amusement, we show in Table 9.2 the order of general unstructured matrices which sparse methods have been used to solve as a function of the date. I think this alone serves to illustrate some of the advances in sparse solution methods over the last 25 years.

Table 9.2: **Order of general sparse matrices solved by direct methods as a function of date**

date	order
1970	200
1975	1000
1980	10000
1985	100000
1990	250000
1995	1000000

The matrix is sparse if the presence of zeros within the matrix enables us to exploit this fact and obtain an economical solution.

There are two main classes of techniques for solving (9.1), iterative methods and direct methods. In a direct method, we use a factored representation and solve the system using these factors in a predetermined amount of memory and time, usually to a high degree of accuracy. In iterative methods, we construct a sequence of approximations to the solution, often the "best" approximation in subspaces of increasing dimension. The work is generally low per iteration but the number of iterations is usually not known *a priori* and may be high, particularly if an accurate solution is required. We consider general aspects of the solution of large sparse linear equations in Section 9.2. We discuss direct methods of solution in Section 9.3 and iterative techniques in Section 9.4 and compare and combine these approaches in Section 9.5. We briefly review matrix diagonalization in Section 9.6 indicating the relationship of techniques used in this case with those used in iterative methods for solving linear equations. We make a few comments on software availability and concluding remarks in Sections 9.7 and 9.8, respectively.

9.2 The solution of linear equations

It is a notational convenience to denote by $\mathbf{A}^{-1}$ the inverse of the matrix $\mathbf{A}$ so that the solution to (9.1) is given by $\mathbf{A}^{-1}\mathbf{b}$. However, there is almost no occasion when it is appropriate to compute the inverse in order to solve a set of linear equations. Even if explicit entries of the inverse are required, for example for sensitivity analysis, there are usually far more computationally efficient ways of doing this than to compute the inverse. For example, the ith column of the inverse can be obtained by solving a set of equations with $\mathbf{e_i}$, the ith column of the identity matrix, as the right-hand side vector and, if specified entries are required, for example the diagonal of $\mathbf{A}^{-1}$, then advantage can be taken of sparsity to compute this efficiently [4].

9.2.1 Accuracy, stability, and conditioning

As a numerical analyst, I am of course concerned about the accuracy of the solution, a concern which I hope is shared by the applications scientist or engineer. Before we continue our discussion on accuracy, it might be useful to first distinguish two concepts which are often confused, namely conditioning and stability. Conditioning is a property of the problem being solved. If the problem is badly conditioned, then small perturbations to the given data could give large changes to the solution, even if it is computed exactly. Stability is a property of the algorithm that is used to effect the solution. An algorithm is *backward* stable if the solution it computes in finite precision arithmetic is the exact solution of a slightly perturbed problem.

A good measure of accuracy would be to measure the difference between computed and exact solutions in some norm, say the l_2 norm, but that is rather difficult since, if you already know the exact solution, there seems little point in going to the trouble of solving the system. A measure which is more easy to compute is the residual $\mathbf{b} - \mathbf{A}\tilde{\mathbf{x}}$, where $\tilde{\mathbf{x}}$ is the computed solution. The residual is a measure of how well your computed solution satisfies the equation. As is common when we do not know (or cannot control) the scaling of the system, we use a relative measure of the residual (dividing by $(||\mathbf{A}||\ ||\tilde{\mathbf{x}}||)$ or some such quantity[2]). This is directly related to the perturbation to the original data that would be needed to ensure that we have computed an exact solution to the perturbed system and is called the backward error, a concept which was pioneered by Jim Wilkinson (for example, [5]) and which revolutionized the thinking of numerical analysts. Now, the backward error is related to the actual (or forward) error through the relationship

$$\text{Forward error} \leq \text{Condition number} \times \text{Backward error} \tag{9.4}$$

where, as we remarked earlier, the *Condition number* is a property of the problem (not the solution technique). There are many different condition numbers [6] and one of the most common is given by

$$\text{Condition number} = ||\mathbf{A}||\ ||\mathbf{A}^{-1}||, \tag{9.5}$$

often denoted by $\kappa(\mathbf{A})$.

A major problem for large sparse systems is that the condition number (even if the original system is scaled) can be far greater than the reciprocal of machine precision. Thus the bound (9.4) indicates that, even if we solve with a backward error of machine precision, our solution may contain no correct digits. It is then a mute point how one decides whether the problem has been solved or not. Usually it is apparent from the underlying problem, so often the applications scientist can judge this better than the numerical analyst. Before you lose all faith in numerical analysis, I should say that this is more alarming than it might at first appear. A simple scaling[3] often helps and sometimes a more appropriate condition number, for example a component-wise one, might give a more realistic bound. However, I should stress that a small (scaled) residual does mean that we have not introduced instability in the solution process. In a sense, we are doing as well as we can even if the solution is far from what was expected.

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[2] When we use norm signs, ||..|| without a suffix, then the actual norm used is not of great importance, although one would normally use consistent norms within a single analysis or computation.

[3] By *scaling* we mean choosing diagonal matrices $\mathbf{D}_1$ and $\mathbf{D}_2$ so that the nonzero entries of the scaled matrix $\mathbf{D}_1\mathbf{A}\mathbf{D}_2$ have similar magnitude.

9.2.2 Effect of symmetry

When an applications scientist or engineer is deciding which algorithm or software to choose, one of the first questions is to ask if the matrix **A** is symmetric (or is Hermitian in the complex case). This makes a crucial difference whether direct or iterative techniques are being used for solution. For direct methods, not only are work and storage nearly halved but, particularly in the commonly occurring positive definite case, more efficient sparse data structures and sparsity based orderings can be used. For iterative methods, not only are the algorithms and software more reliable and robust, but there is often some theory to guarantee convergence. For matrix diagonalization, the normality of symmetric matrices (see Section 9.6) means that robust and accurate methods of determining eigenvalues and eigenvectors exist.

9.3 Direct methods

Direct methods use a factorization of the coefficient matrix to facilitate the solution. The most common factorization for unsymmetric systems is an *LU* factorization where the matrix **A** (or rather a permutation of it) is expressed as the product of a lower triangular matrix **L** and an upper triangular matrix **U**. Thus

$$\mathbf{PAQ} = \mathbf{LU}, \tag{9.6}$$

where **P** and **Q** are permutation matrices. This factorization can then be used to solve the system (9.1) through the two steps:

$$\mathbf{Ly} = \mathbf{Pb}, \tag{9.7}$$

and

$$\mathbf{Uz} = \mathbf{y}, \tag{9.8}$$

whence the solution **x** is just a permutation of the vector **z**, viz.

$$\mathbf{x} = \mathbf{Qz}. \tag{9.9}$$

This use of *LU* factorization to solve systems of equations is usually termed *Gaussian elimination* and indeed the terms are often used synonymously. Another way of viewing Gaussian elimination is as a multistage algorithm which processes the equations in some order. At each stage, a variable is chosen in the equation and is eliminated from all subsequent equations by subtracting an appropriate multiple of that equation from all subsequent ones. The coefficient of the chosen variable is called the *pivot* in Gaussian elimination and the multiple of the pivot row or equation is called the *multiplier*. Clearly, there must be some reordering performed (called *pivoting*) if a pivot is zero but equally pivoting will normally be necessary if the pivot is very small (in fact if the multipliers are large) relative to other entries since then original information could be lost (from adding very large numbers to relatively very small numbers in finite-precision arithmetic) and we could solve a problem quite different from that originally intended. In the sparse case, pivoting is also required to preserve sparsity in the factors. For example, if the matrix **A** is an arrowhead matrix[4], then selecting entry (n, n) as pivot will give dense triangular factors while choosing pivots from the diagonal in any order with entry (n, n) chosen last will give no

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[4] An arrowhead matrix, **A**, has nonzero entries only in positions $a_{ii}, a_{i,n}$, and $\mathrm{a_{n,i}}$, $\mathrm{i} = 1, \ldots, \mathrm{n}$

fill-in (that is, there will be no entries in positions that were not entries in the original matrix). Of course, such a choice could be bad for the numerical criterion just mentioned above. The reconciliation of these possibly conflicting goals of pivoting has been a topic for research. We touch on this briefly below.

If the matrix **A** is symmetric positive definite, it is normal to use the factorization

$$\mathbf{PAP}^T = \mathbf{LL}^T. \tag{9.10}$$

The factorization (9.10) is called a Cholesky factorization. For more general symmetric matrices, the factorization

$$\mathbf{PAP}^T = \mathbf{LDL}^T, \tag{9.11}$$

is more appropriate. For a stable decomposition in the indefinite case, the matrix **D** is block diagonal with blocks of order 1 or 2, and **L** is unit lower triangular.

9.3.1 Phases in solution

In both the case of sparse and dense matrices, the factorization (9.6) is more expensive than the forward elimination and backsubstitution phases, (9.7) and (9.8) respectively. This is less significant if several sets of equations with the same matrix but differing right-hand sides need to be solved. The higher cost of the factorization can then be amortized over the cost of the multiple solutions. In the sparse case, a further distinction is important. Often much of the work concerning handling sparse data structures and choosing pivots can be performed once only for a particular matrix structure and the subsequent factorization of matrices with the same structure can be performed much more efficiently using information from this first factorization. In some cases, the differences in execution time can be quite dramatic as we illustrate in Table 9.3 where there is an order of magnitude difference in time for the three phases. The code `MA48` is a general sparse unsymmetric solver from the Harwell Subroutine Library and GRE 1107 is a test matrix from the Harwell-Boeing Sparse Matrix Collection. The ability to refactorize efficiently subsequent matrices is not present in all software packages but is very important particularly when solving nonlinear systems when the Jacobian will retain the same structure although the numerical values change.

Table 9.3: **Execution times (in seconds) for code `MA48` for matrix GRE 1107 on a single processor of a CRAY Y-MP**

First factorization	.66
Subsequent factorizations	.075
Back and forward substitution	.0068

9.3.2 Sparsity preservation and numerical stability

In the sparse case, it is crucial that the permutation matrices of (9.6) are chosen to preserve sparsity in the factors as well as to maintain stability and many algorithms have been developed to achieve this. For general unsymmetric matrices the most popular method is called "Markowitz with *threshold pivoting*". Threshold pivoting ensures that pivots are within a certain threshold of the largest entry in the row or column. The threshold is often an input parameter and a typical value for it is 0.1. We control sparsity by choosing the pivot to be an entry satisfying the threshold criterion that has the fewest product of number of other entries in its row and column. The suggestion of using this sparsity control is due to [7]. In the symmetric case, the Markowitz analogue is *minimum degree* where one chooses as pivot a diagonal entry with the least number of entries in its row.

9.3.3 Arithmetic complexity

Although the LU factorization has a similar $\mathcal{O}(n^3)$ complexity[5] to matrix inversion for dense systems (and storage requirements of $\mathcal{O}(n^2)$), the complexity of the factorization process and storage requirements for sparse matrices depend on the structure and can be significantly less. For example the LU factorization of a tridiagonal matrix can be done in $\mathcal{O}(n)$ operations whereas the calculation of the inverse is at best $\mathcal{O}(n^2)$. Furthermore, the storage for the factors of a tridiagonal matrix are the same as the original matrix ($3n - 2$ reals) but the inverse of a tridiagonal matrix is dense. In fact, if we consider structure only and do not allow numerical cancellation, the inverse of an irreducible sparse matrix[6] is always dense [8]. An archetypal example, is a five-diagonal matrix[7] as obtained, for example, from the finite-difference discretization of a two-dimensional Laplacian. If the discretization has k grid points in each direction (so that the order of the matrix is k^2), the LU factorization would require $\mathcal{O}(k^6)$ if considered as a dense system but $\mathcal{O}(k^4)$ if considered banded (and the storage requirement reduced from k^4 to k^3). Although this figure is often quoted when comparing the complexity of LU factorization with other methods on such matrices, by using a nested dissection ordering algorithm, the work and storage can be reduced to $\mathcal{O}(k^3)$ and $\mathcal{O}(k^2 \log k)$ respectively. The bad news is that one can prove that, for a wide range of matrices including the five-diagonal one, this is asymptotically the best that can be done for any direct method based on LU factorization.

9.3.4 Indirect addressing and the use of the BLAS

For arbitrarily structured sparse matrices, complicated data structures are needed for efficient execution (for example, [9]). Although this is hidden from the user of the sparse code, it can significantly affect the efficiency of the computation. Even for computers with hardware indirect addressing, access to data of the form `A(IND(I)), I = 1, K` carries a heavy penalty in terms of additional memory traffic and non-localization of data. When this is added to the fact that most loops are of the order of number of nonzero entries in a row rather than the order of the system, general sparse codes can perform particularly badly on some high performance computers relative to their dense counterpart. Much recent research on sparse direct techniques has been to develop algorithms and codes that use the same kernels as dense codes at the innermost loops.

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[5] See, however, the comments on Strassen's algorithm which follow.

[6] A matrix is irreducible if it is not possible to reorder the matrix rows and columns so the reordered form has a nontrivial block triangular form.

[7] By five-diagonal matrix, we mean a matrix that has nonzeros only in five diagonals.

The BLAS, or Basic Linear Algebra Subprograms, are well established standard operations on dense matrices and vectors, and include computations such as scalar products, solution of triangular systems, and multiplication of two matrices ([10], [11], [12]). The important thing is that the interface to each subprogram has been standardized and most vendors have developed optimized code for these kernels. For example, the matrix-matrix multiplication routine (`_GEMM`) performs at close to peak performance on many computers, even those with quite sophisticated architectures involving vector processing, memory hierarchy, caches etc. Much of the recent work in dense linear algebra has centred round the use of these kernels. However, in spite of some early work by [13] and others, it is only quite recently that it has become appreciated that these dense linear algebra kernels can be used effectively within direct methods for sparse matrices.

Table 9.4: **Performance of `_GEMM` kernel in Mflop/s on a range of machines (single processor performance)**

Machine	*Peak*	`_GEMM`
Meiko CS2-HA	100	88
IBM SP-2	266	213
Intel PARAGON	75	68
DEC Turbo Laser	600	450
CRAY 2	459	449
CRAY YMP	333	313

We show, in Table 9.4, the performance of the Level 3 BLAS kernel `_GEMM` on a range of computers with various floating-point chips and memory organizations. In many cases, this kernel attains about 90% or more of the peak performance of the chip and in every case more than 75% of peak is achieved. This remarkable performance is obtained by the fact that a (dense) matrix-matrix multiply performs $2n^3$ arithmetic operations but only requires $3n^2$ data references. This enables data that is brought into the memory hierarchy (say onto an on-chip cache) to be reused, thus amortizing the cost of transferring it from main memory or even further afield. Since the memory level closest to the floating-point unit can usually supply data at the same speed as the unit computes, we can then get close to the speed of the floating-point unit.

As a footnote to the complexity issue, we should record the fact that methods have been developed for multiplying dense matrices in $\mathcal{O}(n^\alpha)$ operations, where $\alpha < 3$, based on Strassen's method [14]. `_GEMM` has been implemented using this algorithm (for example, [15]) and so the use of this kernel in dense Gaussian elimination can reduce the complexity accordingly. Note that the added complexity of Strassen's algorithm and the need to pay more care to stability [16] means that this is not the panacea to the "n^3 problem". Also the lowest value of α that has been so far obtained is 2.376 so that dense matrix computations still quickly become infeasible when the matrix order becomes very large.

The trick is now to develop sparse matrix techniques that can take advantage of these fast dense matrix kernels. Of course, it is possible just to solve the sparse system using a code for dense systems, and some people have advocated this approach arguing that the greater "peak" speed and memory of modern computers makes this feasible. I must stress that the complexity discussions we had earlier makes this really non-viable for all but the smallest sparse matrices. We illustrate the wide difference in execution times for sparse and dense codes on sparse matrices by the results in Table 9.5. Although there are now much faster machines than a CRAY Y-MP, the matrices used in this table are quite small by current standards.

Table 9.5: **Comparison between `MA48` (a sparse code) and LAPACK (`SGESV`) (a dense code) on a range of matrices from the Harwell-Boeing Sparse Matrix Collection.** Times are for factorization and solution (in seconds on one processor of a CRAY Y-MP)

Matrix	Order	Entries	`MA48`	`SGESV`
FS 680 3	680	2646	0.06	0.96
PORES 2	1224	9613	0.54	4.54
BCSSTK27	1224	56126	2.07	4.55
NNC1374	1374	8606	0.70	6.19
WEST2021	2021	7353	0.21	18.88
ORSREG 1	2205	14133	2.65	24.25
ORANI678	2529	90158	1.17	36.37

9.3.5 Frontal and multifrontal methods

A more viable approach is to order the sparse matrix so that its nonzero entries are clustered near the diagonal (called bandwidth minimization) and then regard the matrix as banded, treating zeros within the band as nonzero. However, this is normally too wasteful as even the high computational rate of the Level 3 BLAS does not compensate for the extra work on the zero entries. A variable band format is used to extend the range of applicability of this technique. A related, but more flexible scheme, is the frontal method which owes its origin to computations using finite elements.

Here we assume that $\mathbf{A}$ is of the form

$$\mathbf{A} = \sum_{l=1}^{m} \mathbf{A}^{[l]}$$

where each element matrix $\mathbf{A}^{[l]}$ has nonzeros in only a few rows and columns and is normally held as a small dense matrix representing contributions to $\mathbf{A}$ from element l. If a_{ij} and $a_{ij}^{[l]}$ denote the (i,j)th entry of $\mathbf{A}$ and $\mathbf{A}^{[l]}$, respectively, the basic assembly operation when forming $\mathbf{A}$ is of the form

$$a_{ij} \Leftarrow a_{ij} + a_{ij}^{[l]}. \tag{9.12}$$

It is evident that the basic operation in Gaussian elimination

$$a_{ij} \Leftarrow a_{ij} - a_{ip}[a_{pp}]^{-1}a_{pj} \tag{9.13}$$

may be performed as soon as all the terms in the triple product (9.13) are *fully summed* (that is, are involved in no more sums of the form (9.12)). The assembly and Gaussian elimination processes can therefore be interleaved and the matrix $\mathbf{A}$ is never assembled explicitly. Variables that are internal to a single element can be immediately eliminated (called *static condensation*) and this can be extended to a submatrix from a set of elements, that is a sum of several element matrices. In this scheme, all intermediate working can be performed within a dense matrix, termed the *frontal matrix*, whose rows and columns correspond to variables that have not yet been eliminated but occur in at least one of the elements that have been assembled.

We can partition the frontal matrix, $\mathbf{F}$, as:

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}_{11} & \mathbf{F}_{12} \\ \mathbf{F}_{21} & \mathbf{F}_{22} \end{bmatrix} \tag{9.14}$$

where the fully summed variables correspond to the rows and columns of the block $\mathbf{F}_{11}$, from where the pivots can be chosen. The kernel computation in a frontal scheme is then of the form

$$\mathbf{F}_{22} \leftarrow \mathbf{F}_{22} - \mathbf{F}_{21}\mathbf{F}_{11}^{-1}\mathbf{F}_{12} \tag{9.15}$$

and can be performed using Level 3 BLAS. (We note that this expression is notational and the inverse of $\mathbf{F}_{11}$ is not explicitly calculated.)

The frontal method can be easily extended to non-element problems since any set of rows of a sparse matrix can be held in a rectangular array whose number of columns is equal to the number of columns with nonzero entries in the selected rows. A variable is regarded as fully summed whenever the equation in which it last appears is assembled. These frontal matrices can often be quite sparse but are suitable for computations involving Level 3 dense BLAS. A full discussion of the equation input can be found in [17].

If the frontal scheme is combined with an ordering to preserve sparsity and reduce the number of floating-point operations and if a new frontal matrix can be formed independently of already existing frontal matrices, we can develop a scheme that combines the benefits of using Level 3 BLAS with the gains from using sparsity orderings. This is developed in *multifrontal schemes* where the computation can be viewed as a tree, whose nodes represent computations of the form (9.15) and whose edges represent the transfer of data from the child to the parent (data of the form of the $\mathbf{F}_{22}$ matrices generated by (9.15)). Another approach that combines sparse ordering schemes with higher level dense BLAS is the supernodal approach (for example, [18]).

9.3.6 Parallelization of direct methods

In the late 80's and early 90's, it was almost impossible to obtain research funding in linear algebra unless parallelism was mentioned in the abstract if not the title. The topic was also embraced by computer scientists who could theorize on what the complexity of elimination techniques might be on a range of hypothetical computers and exotic parallel metacomputers with $\mathcal{O}(n^p)$ processors. I daresay some of this work was useful as other than an intellectual exercise, but the last few years have seen a more mature study of realistic parallel algorithms that can be implemented on actual available computers and can (and are sometimes) even used by applications people or industry.

Although algorithms and software for the parallel solution of dense systems of equations have been developed (for example, the ScaLAPACK package of [19]), the irregularity of sparse matrix structures makes it much more difficult to efficiently parallelize methods for sparse equations. The PARASOL Project is an ambitious attempt in this direction.

PARASOL[8] is an ESPRIT IV Long Term Research Project (No 20160) for "An Integrated Environment for Parallel Sparse Matrix Solvers". The main goal of this Project, which started on January 1 1996, is to build and test a portable library for solving large sparse systems of equations on distributed memory systems. There are twelve partners in five countries, five of whom are code developers, five end users, and two software houses. The software is written in Fortran 90 and uses MPI for message passing. The solvers being developed in this consortium are: two domain decomposition codes by Bergen and ONERA, a multigrid code by GMD, and a parallel multifrontal method (called MUMPS) by CERFACS and RAL. The final library will be in the public domain.

It is common, when examining implementations on parallel computers, to stress the speedup, or how many times faster the application runs on multiple processors than a single processor, although it is recognized that a more important measure is the execution time relative to the fastest method on a uniprocessor. However, an often more important reason for parallel computation is the the benefit of having access to more memory. This is particularly true on machines which have memory entirely local to each processor and which use message passing to share data between processors. In this case, the more processors; the more memory. A side effect of this is that it may only be possible to run a large problem on several processors so a comparison with a uniprocessor code is inappropriate. Furthermore, the memory system may be inefficient when stressed (for example, because of memory paging) and so the speedup may be superlinear. We illustrate this amusing effect by some runs of a parallel multifrontal code from the PARASOL Project on a PARASOL test problem on an IBM SP2 and an SGI Origin 2000 in Table 9.6. The speedups on the Origin reflect the true parallelism of the software, whereas those on the SP2 include a memory effect.

9.4 Iterative methods

In contrast to direct methods, iterative methods do not normally modify the matrix and do not form any representation of the inverse. Furthermore, most iterative methods do not require the matrix to be represented explicitly, sometimes it is sufficient to be able to form the product of the matrix with a vector, although this may restrict the preconditioning available (see Section 9.4.1).

Iteration techniques such as successive approximation have been around since the first days of scientific computing and the early iterative techniques for solving sparse linear equations were based on such approaches (Gauss-Seidel, SOR etc). While these methods are still used (for example, as smoothers in multigrid techniques), it is true to say that most modern methods for the iterative solution of sparse equations are based on Krylov sequences of the form

$$sp\{\mathbf{v}, \mathbf{A}\mathbf{v}, \mathbf{A}^2\mathbf{v}, ...\}, \tag{9.16}$$

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[8] For more information on the PARASOL project, see the web site at `http://www.genias.de/parasol`.

Table 9.6: **Results for the symmetric version of the MUMPS code on** CRANKSEG2.

Machine	Working processors	Time for factorization
SP2	16	1045.3
	24	457.3
	32	139.7
Origin	1	635.4
	2	411.0
	3	275.7
	4	220.4
	5	175.1
	6	158.3
	7	142.9
	8	135.7

with the approximate solution at each step the “best” solution that lies in the subspace of increasing dimension. What constitutes “best” determines which of the many methods is defined.

The residual at the i-th iteration of an iterative method can be expressed as

$$\mathbf{r^{(i)}} = P_i(\mathbf{A})\mathbf{r^{(0)}}, \tag{9.17}$$

where P_i is a polynomial such that $P_i(0) = 1$. If we expand $\mathbf{r^{(0)}}$ in terms of the eigenvectors of $\mathbf{A}$ we see that we want P_i to be small on the eigenvalues of $\mathbf{A}$ so that the spectrum of $\mathbf{A}$ is crucial in determining how quickly our method converges. For example, if there are many eigenvalues close to zero or if the spectrum is widely distributed, the degree of polynomial will have to be high in order to be small on all eigenvalues and so the number of iterations required will be large.

A major feature of most Krylov based methods for symmetric systems are that they can be implemented using short term recurrences which means that only a few vectors of length n need be kept and the amount of computation at each stage of the iterative process is modest. However, Faber and Manteuffel (1984) have shown that, for general matrices, one must either lose the cheap recurrences or lose the minimization property. Thus for the solution of general unsymmetric systems, the balance between these, added to the range of quantities that can be minimized and the differing norms that can be used, has led to a veritable alphabet soup of methods [20], for example GMRES(k), CGS, Bi-CGSTAB(ℓ), TFQMR, FGMRES, GMRESR, ...

9.4.1 Preconditioning

The key to developing iterative methods for the solution of realistic problems lies in preconditioning, where by this we mean finding a matrix $\mathbf{K}$ such that

1. $\mathbf{K}$ is an approximation to $\mathbf{A}$.

2. $\mathbf{K}$ is cheap to construct and store.

3. $\mathbf{Kx} = \mathbf{b}$ is much easier to solve than the system (9.1).

We then solve the preconditioned system

$$\mathbf{K}^{-1}\mathbf{Ax} = \mathbf{K}^{-1}\mathbf{b}, \tag{9.18}$$

where we have chosen $\mathbf{K}$ so that our iterative method converges more quickly when solving equation (9.18) than equation (9.1). Lest this seem too much of a black art (which to some extent it is), if $\mathbf{K}$ were chosen as the product of the factors $\mathbf{LU}$ from an LU factorization (admittedly violating point 2 above), then the preconditioned matrix $\mathbf{B} = \mathbf{K}^{-1}\mathbf{A}$ would be the identity matrix and any sane iterative method would converge in a single iteration. From our earlier discussion, we would like the preconditioned matrix $\mathbf{B}$ to have a better distribution of eigenvalues than $\mathbf{A}$.

The preconditioning can also be applied as a right-preconditioning $\mathbf{AK}^{-1}$ or as a two-sided preconditioning $\mathbf{K}_1^{-1}\mathbf{AK}_2^{-1}$, when the matrix $\mathbf{K}$ can be expressed as a product $\mathbf{K}_1\mathbf{K}_2$. Common preconditioners include using the diagonal of $\mathbf{A}$ or a partial or incomplete factorization of $\mathbf{A}$. A recent simple discussion of the merits of different forms of preconditioners and their implementation can be found in the report [21] that is a preprint of a chapter in a forthcoming book [22].

A very interesting aspect of this is that convergence can occur in very few iterations if the eigenvalues are well clustered. This is, of course, true whether the matrix is dense or sparse. In the dense case, a direct method will require $\mathcal{O}(n^3)$ work whereas a single matrix vector multiplication only $\mathcal{O}(n^2)$. Thus, if our iterative method converges in only a few iterations, it may be a very attractive method for solving the dense system. An example where dense systems with well clustered eigenvalues are found is given by [23]. However, as in the case of sparse systems, preconditioning is normally needed to obtain a good eigenvalue distribution. This is less attractive in the dense case because another n^2 multiplications are required and, if it is required to solve for the preconditioning matrix, our subproblem is as hard as the original problem. It is sometimes possible, however, to develop sparse preconditioning matrices for the dense problem (for example, [24]) so that the cost of this preconditioning is small compared to the multiplication by the original matrix. In some cases, the structure of the problem can be used to reduce the matrix-vector multiplication itself, for example by using multipole methods [25].

9.4.2 Parallelization of iterative methods

In contrast to direct methods, each step of an iterative method is relatively easy to parallelize since the only numerical computations involved are:

- $\mathbf{Av}$
- $\mathbf{v}^T\mathbf{w}$

- $\mathbf{v} - \alpha \mathbf{w}$

and, for the preconditioning:

- $\mathbf{K}^{-1}\mathbf{v}$

The first operations can be performed with high efficiency on parallel computers, for example [26], although scalar products require synchronization and much communication. The achilles heel for performance is, however, usually in the efficient implementation of the preconditioning, on which much research is still being done (see for example, [22]). We should add that it is vital that the preconditioner is effective in reducing the number of iterations because, if the convergence is so slow as to be meaningless, no amount of parallelism can make it viable.

9.5 Direct or iterative or ?

I am often asked whether it is better to use an iterative or a direct method to solve a set of linear equations. The answer is often quite simple, and not just because of the predilection of my research interest. One should use a direct method! This is even more true if you have several right-hand sides to solve with the same coefficient matrix. However, since your computer is unlikely to be blessed with an infinite amount of memory (unless you are a theoretician from the 80's), the range of problems for which such a technique is applicable is limited, significantly so if your underlying problem is three-dimensional. In such cases, one has to resort to an iterative method. However, since for all but the simplest cases, your chosen iterative method (even with a standard preconditioner) is unlikely to converge ... what do you do?

The answer is to use a technique that combines elements of both direct and iterative methods. Sophisticated preconditioners come into this category. The most obvious method to combine these approaches is the block Jacobi method where the matrix is treated as a block matrix, the solution of the subproblems corresponding to the diagonal blocks are performed using a direct method, and the system is solved using a block Jacobi algorithm. Clearly this inherits much of the parallelism of the point case but should have better convergence properties. Indeed a variant corresponding to using a block Jacobi scheme on the normal equations, termed the block Cimmino algorithm, has proven quite effective (for example, [27]). As in the point case, we can sacrifice parallelism a little and gain faster convergence through the use of a block Gauss-Seidel method. The counterpart to block Cimmino is then block Kacmarz (for example, [28]).

In the framework of the solution of partial differential equations, a more general technique for combining direct and iterative methods is to use domain decomposition [29, 30], where the problem is divided into separate domains (either overlapping or non-overlapping) and the local problems can be solved using direct methods, which of course is trivial to do in parallel since these subproblems are decoupled. In the case of non-overlapping domains, usually the main issue is the solution of the problem for the interface variables. It is normal to use an iterative method for this but the main problem is then to define a preconditioner, particularly if the matrix corresponding to the interface problem is not computed explicitly.

One way in which direct methods can be used as preconditioners for iterative methods are to perform only a partial factorization, as is the case for ILU(k) preconditioners, where a limited amount of fill-in is allowed to the matrix factors so that an incomplete factorization is performed. Another approach is to perform a "full" factorization but one of a reduced or simpler problem to the original, for example for a simpler differential equation than the original.

Multigrid methods have become very popular in recent years largely because of their provably optimal performance on simple elliptic problems. In these techniques, a sequence of grids is used. The solution is required on the finest grid. A few passes of a simple iterative method are performed and the residual is projected onto the next coarser grid. A correction is obtained by projecting back the solution of the residual equations on this coarser grid to the finer grid. Since the solution of the residual equations can be performed using an even coarser grid, multiple grids can be used. The essence of the method is that the simple iterative method (or smoother) tends to efficiently remove error components that vary as quickly as the grid size and the use of coarser grids enables the smoother components of the error to be reduced. While the individual sweeps of the smoothers can be parallelized, it is harder to parallelize across the grids but there has been some recent work on this, for example by the PARASOL Project mentioned earlier.

9.6 Matrix diagonalization

What physicists call matrix diagonalization, numerical analysts call the eigenproblem. In the case of small matrices, there are many techniques for both symmetric and unsymmetric matrices that involve computing transformations of the matrix to diagonal form usually in a two-step process, the first step transforming the matrix to tridiagonal or Hessenberg form, respectively. Although the use of high Level BLAS in these computations improves their efficiency, the transformations involved destroy sparsity in a way that is not normally as recoverable as in the case of LU factorization. Additionally, in the large sparse case, normally only a few eigenvalues and eigenvectors are required. Thus for large sparse matrices, we use other methods for obtaining the eigenvalues.

In fact the basis of eigensolution techniques for large sparse matrices is the same as we just discussed for the iterative solution of sparse equations, namely the Krylov sequence (9.16). Clearly, this is a generalization of the classical power method for computing eigenvalues and eigenvectors, but differs significantly because the previous powers are taken into account so that the size of the subspace increases as iterations are performed. Additionally, in the Krylov based methods, we are free to choose appropriate bases for the subspaces.

In our brief discussion that follows, we will be concerned with the standard eigenproblem (9.3), although we note that normally the generalized problem (9.2) is first converted to a standard one, for example on a matrix of the form $(\mathbf{A} - \sigma\mathbf{B})^{-1}\mathbf{B}$ or $\mathbf{L}^{-1}\mathbf{A}\mathbf{L}^{-T}$, when $\mathbf{B} = \mathbf{L}\mathbf{L}^T$ is symmetric positive definite.

Whereas for linear systems, we seek solutions of the form

$$\mathbf{Q}_k\mathbf{y}_k,$$

where $\mathbf{Q}_k = [\mathbf{q}_1\mathbf{q}_2....\mathbf{q}_k]$ is the basis of the Krylov subspace of dimension k, for the eigenproblem, we solve a reduced eigenproblem for the projected subspace

$$\mathbf{Q}_k^*\mathbf{A}\mathbf{Q}_k. \tag{9.19}$$

For the eigenproblem, we can again use preconditioning techniques to accelerate convergence. In this case, the subspaces are generated for a simple function of $\mathbf{A}$ so that the eigenvalues required are better represented in subspaces of the form (9.19) of low dimension.

Since the kernels of Krylov subspace methods for finding eigenvalues are exactly those listed for the iterative solution of linear equations at the end of Section 9.4, eigenvalue calculations are also relatively easy to parallelize with possible bottlenecks in preconditioning.

A recently investigated phenomenon is that of non-normality [31]. Formally a matrix is normal if

$$\mathbf{A}^*\mathbf{A} = \mathbf{A}\mathbf{A}^*$$

and so all symmetric (or Hermitian) matrices are normal. The most important feature of normal matrices are that there exists a unitary matrix $\mathbf{Q}$ such that $\mathbf{Q}^*\mathbf{A}\mathbf{Q}$ is diagonal. This in turn means that the eigenproblem is well-conditioned in the sense that a small perturbation to the matrix produces a small perturbation of the eigenvalues. However, for non-normal but diagonalizable matrices the diagonalization $\mathbf{X}^{-1}\mathbf{A}\mathbf{X}$, implies nothing about the condition number, $\kappa(\mathbf{X})$, of $\mathbf{X}$, so that, by the Bauer-Fike theorem, if

$$\mathbf{X}^{-1}\mathbf{A}\mathbf{X} = \mathbf{D} = \mathrm{diag}\{\lambda_1, ..., \lambda_\mathrm{n}\}$$

and μ is an eigenvalue of the perturbed matrix $\mathbf{A} + \mathbf{E}$, then

$$\min_{\lambda} |\lambda - \mu| \leq \kappa(\mathbf{X})||\mathbf{E}||.$$

A similar result holds for non-diagonalizable matrices.

This means that even a matrix very close to $\mathbf{A}$ might have very different eigenvalues. This phenomenon can be viewed in a diagram containing contours of the resolvent

$$||(\mathbf{A} - \lambda\mathbf{I})^{-1}||$$

and pseudo-eigenvalues are defined by regions in the plane where the resolvent is large. There is now some debate about whether physical processes are governed by pseudo-eigenvalues rather than eigenvalues but certainly one should be very wary of making a qualitative judgement of a process or its stability on the strength of a single or few eigenvalues [32]. One should note that a complex symmetric matrix is not Hermitian and can be non-normal.

9.7 Sources of Software

The origins of much specialist work in numerical software stem from the requirement of computational physicists and chemists, and libraries and collections of software were developed to avoid duplication of effort and provide a sound base of portable codes. I would not advise the applications scientist or engineer to try to reverse this historical trend by coding his or her own matrix algorithm, even using a numerical recipes crib sheet.

There are many sources of software for sparse matrices, from the do-it-yourself approach of the Templates book for iterative methods [33] (a similar one for eigenproblems is forthcoming), to supported proprietary codes as are present in the Harwell Subroutine Library, `http://www.dci.rl.ac.uk/Activity/HSL` [34]. Some codes are available through `netlib`, `http://www.netlib.org`, and others from the Web pages of the researchers developing the code. The problem with the latter source is that, in addition to a lack of quality control, the researcher in question will often have no compunction against editing the code almost as you are downloading it.

We discuss sources of sparse matrix software in [35] and a recent report by [36] discusses, in some detail, software for iterative methods for solving linear systems. The reports by [37] ([38], [37]) discuss sparse eigenvalue software.

9.8 Brief Summary

We have presented a few obvious, and hopefully some less obvious, comments on the solution of large sparse systems and large eigenproblems. We have emphasized the similarity between iterative solution techniques and matrix diagonalization procedures, and indicated briefly how direct and iterative methods can be combined to solve really large problems. We see considerable promise in both frontal and multifrontal methods on machines with memory hierarchies or vector processors and reasonable possibilities for exploitation of parallelism by multifrontal methods. A principal factor in attaining high performance is the use of dense matrix computational kernels, which have proved extremely effective in the dense case.

Finally, we have tried to keep the narrative flowing in this presentation by avoiding an excessive number of references. For such information, we recommend, for linear systems, the recent review by [35], where 215 references are listed. [39] has written a book on large-scale eigenproblems with an emphasis on computational aspects and more recent references on iterative solution of equations and eigenproblems can be found in [40] and [41] respectively.

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References

[1] Duff, I. S., Grimes, R. G. and Lewis, J. G. (1989), 'Sparse matrix test problems', *ACM Trans. Math. Softw.* **15**(1), 1–14.

[2] Duff, I. S., Grimes, R. G. and Lewis, J. G. (1997), The Rutherford-Boeing Sparse Matrix Collection, Technical Report RAL-TR-97-031, Rutherford Appleton Laboratory. Also Technical Report ISSTECH-97-017 from Boeing Information & Support Services and Report TR/PA/97/36 from CERFACS, Toulouse.

[3] Anderson, E., Bai, Z., Bischof, C., Demmel, J., Dongarra, J., DuCroz, J., Greenbaum, A., Hammarling, S., McKenney, A., Ostrouchov, S. and Sorensen, D. (1995), *LAPACK Users' Guide, second edition*, SIAM Press.

[4] Erisman, A. M. and Tinney, W. F. (1975), 'On computing certain elements of the inverse of a sparse matrix', *Communications of the Association for Computing Machinery* **18**, 177–179.

[5] Wilkinson, J. H. (1961), 'Error analysis of direct methods of matrix inversion', *J. ACM* **8**, 281–330.

[6] Higham, N. J. (1996), *Accuracy and Stability of Numerical Algorithms*, SIAM Press, Philadelphia.

[7] Markowitz, H. M. (1957), 'The elimination form of the inverse and its application to linear programming', *Management Science* **3**, 255–269.

[8] Duff, I. S., Erisman, A. M., Gear, C. W. and Reid, J. K. (1988), 'Sparsity structure and Gaussian elimination', *SIGNUM Newsletter* **23**(2), 2–8.

[9] Duff, I. S., Erisman, A. M. and Reid, J. K. (1986), *Direct Methods for Sparse Matrices*, Oxford University Press, Oxford, England.

[10] Lawson, C. L., Hanson, R. J., Kincaid, D. R. and Krogh, F. T. (1979), 'Basic linear algebra subprograms for Fortran usage', *ACM Trans. Math. Softw.* **5**, 308–323.

[11] Dongarra, J. J., Du Croz, J. J., Hammarling, S. and Hanson, R. J. (1988), 'An extented set of Fortran Basic Linear Algebra Subprograms', *ACM Trans. Math. Softw.* **14**, 1–17.

[12] Dongarra, J. J., Du Croz, J., Duff, I. S. and Hammarling, S. (1990), 'A set of Level 3 Basic Linear Algebra Subprograms.', *ACM Trans. Math. Softw.* **16**, 1–17.

[13] Duff, I. S. (1981), The design and use of a frontal scheme for solving sparse unsymmetric equations, *in* J. P. Hennart, ed., 'Numerical Analysis, Proceedings of 3rd IIMAS Workshop. Lecture Notes in Mathematics 909', Springer Verlag, Berlin, pp. 240–247.

[14] Strassen, V. (1969), 'Gaussian elimination is not optimal', *Numerische Mathematik* **13**, 354–356.

[15] Douglas, C. C., Heroux, M., Slishman, G. and Smith, R. M. (1992), GEMMW: A portable level 3 BLAS Winograd variant of Strassen's matrix-matrix multiply algorithm, Technical Report RC 18026 (79130), IBM T. J. Watson Research Centre, P. O. Box 218, Yorktown Heights, NY 10598.

[16] Higham, N. J. (1990), 'Exploiting fast matrix multiplication within the Level 3 BLAS', *ACM Trans. Math. Softw.* **16**, 352–368.

[17] Duff, I. S. (1984), 'Design features of a frontal code for solving sparse unsymmetric linear systems out-of-core', *SIAM J. Scientific and Statistical Computing* **5**, 270–280.

[18] Demmel, J. W., Eisenstat, S. C., Gilbert, J. R., Li, X. S. and Liu, J. W. H. (1995), A supernodal approach to sparse partial pivoting, Technical Report UCB//CSD-95-883, Computer Science Division, U. C. Berkeley, Berkeley, California.

[19] Blackford, L. S., Choi, J., Cleary, A., D'Azevedo, E., Demmel, J., Dhillon, I., Dongarra, J., Hammarling, S., Henry, G., Petitet, A., Stanley, K., Walker, D. and Whaley, R. C. (1997), *ScaLAPACK Users' Guide*, SIAM Press.

[20] Saad, Y. (1996), *Iterative methods for sparse linear systems*, PWS Publishing, New York, NY.

[21] Duff, I. S. and van der Vorst, H. A. (1998), Preconditioning and parallel preconditioning, Technical Report RAL-TR-1998-052, Rutherford Appleton Laboratory.

[22] Dongarra, J. J., Duff, I. S., Sorensen, D. C. and van der Vorst, H. A. (1998), *Numerical Linear Algebra for High-Performance Computers*, SIAM Press, Philadelphia.

[23] Rahola, J. (1996), Efficient solution of dense systems of linear equations in electromagnetic scattering calculations, PhD Thesis, CSC Research Reports R06/96, Center for Scientific Computing, Department of Engineering Physics and Mathematics, Helsinki University of Technology.

[24] Alléon, G., Benzi, M. and Giraud, L. (1997), 'Sparse approximate inverse preconditioning for dense linear systems arising in computational electromagnetics', *Numerical Algorithms* **16**(1), 1–15.

[25] Rahola, J. (1998), Experiments on iterative methods and the fast multipole method in electromagnetic scattering calculations, Technical Report TR/PA/98/49, CERFACS, Toulouse, France.

[26] Erhel, J. (1990), 'Sparse matrix multiplication on vector computers', *Int J. High Speed Computing* **2**, 101–116.

[27] Arioli, M., Duff, I. S., Ruiz, D. and Sadkane, M. (1995), 'Block Lanczos techniques for accelerating the Block Cimmino method', *SIAM J. Scientific Computing* **16**(6), 1478–1511.

[28] Bramley, R. and Sameh, A. (1992), 'Row projection methods for large nonsymmetric linear systems', *SIAM J. Scientific and Statistical Computing* **13**, 168–193.

[29] Chan, T. F. and Mathew, T. P. (1994), *Domain Decomposition Algorithms*, Vol. 3 of *Acta Numerica*, Cambridge University Press, Cambridge, pp. 61–143.

[30] Smith, B., Björstad, P. and Gropp, W. (1996), *Domain Decomposition, Parallel Multilevel Methods for Elliptic Partial Differential Equations*, 1st edn, Cambridge University Press, New York.

[31] Chaitin-Chatelin, F. and Frayssé, V. (1996), *Lectures on Finite Precision Computations*, SIAM Press, Philadelphia.

[32] Trefethen, L. N., Trefethen, A. E., Reddy, S. C. and Driscoll, T. A. (1993), 'Hydrodynamics stability without eigenvalues', *Science* **261**, 578–584.

[33] Barrett, R., Berry, M., Chan, T., Demmel, J., Donato, J., Dongarra, J., Eijkhout, V., Pozo, R., Romine, C. and van der Vorst, H., eds (1993), *Templates for the Solution of Linear Systems: Building Blocks for Iterative Methods*, SIAM, Philadelphia.

[34] HSL (1996), *Harwell Subroutine Library. A Catalogue of Subroutines (Release 12)*, AEA Technology, Harwell Laboratory, Oxfordshire, England. For information concerning HSL contact: Dr Scott Roberts, AEA Technology, 477 Harwell, Didcot, Oxon OX11 0RA, England (tel: +44-1235-432682, fax: +44-1235-432023, email: Scott.Roberts@aeat.co.uk).

[35] Duff, I. S. (1997), Sparse numerical linear algebra: Direct methods and preconditioning, *in* I. S. Duff and G. A. Watson, eds, 'The State of the Art in Numerical Analysis', Oxford University Press, Oxford, pp. 27–62.

[36] Eijkhout, V. (1998), 'Overview of iterative linear system solver packages', *NHSE Review.* `http://www.nhse.org/NHSEreview/98-1.html`.

[37] Lehoucq, R. B. and Scott, J. A. (1996*b*), An evaluation of subspace iteration software for sparse nonsymmetric eigenproblems, Technical Report RAL-TR-96-022, Rutherford Appleton Laboratory.

[38] Lehoucq, R. B. and Scott, J. A. (1996*a*), An evaluation of Arnoldi based software for sparse nonsymmetric eigenproblems, Technical Report RAL-TR-96-023, Rutherford Appleton Laboratory.

[39] Saad, Y. (1992), *Numerical Methods for Large Eigenvalue Problems*, Manchester University Press, Manchester, UK.

[40] Golub, G. H. and van der Vorst, H. A. (1996), Closer to the solution: Iterative linear solvers, *in* I. S. Duff and G. A. Watson, eds, 'The State of the Art in Numerical Analysis', Oxford University Press, Oxford, pp. 63–92.

[41] van der Vorst, H. A. and Golub, G. H. (1996), 150 years old and still alive: Eigenproblems, *in* I. S. Duff and G. A. Watson, eds, 'The State of the Art in Numerical Analysis', Oxford University Press, Oxford, pp. 93–119.