

Ψ_k Network

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

Number 10

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Editor: Z. (Dzidka) Szotek

Proposal: ERB4050PL930589

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Editorial

In this *Newsletter* we have a new section called **Presenting Other HCM Networks** which contains an article by W.M.C. Foulkes et al. on "*Quantum Monte Carlo Calculations for Real Solids*". In it readers can also find information on the *Quantum Monte Carlo HCM Network* of which the authors are part. The intention was to give our readers a flavour of current scientific issues and activities of other HCM networks.

In the **Highlight of the Month Section**, which follows the above article and is the last item of this *Newsletter*, Christiane Koenig (the spokesperson of the *Molecules and Organic Solids Working Group* of our ψ_k - *Network*) and C. Hoerner elaborate on topics of current interest of this Working Group. The article is entitled "*Mixed-stack organic charge-transfer compounds*".

The **Editorial** is followed by the section **News from the Network**, where some current issues of the *Network* are mentioned.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits. Straight after the reports there are the announcements of a **Ph. D. position** in Dresden, a **postdoc position** in Oxford University, and a joint **Ph. D. case studentship** between the Sheffield University and Daresbury Laboratory. These are followed by the programme of the ERC conference on "**Itinerant Magnetism**" which will take place in Lunteren (The Netherlands) from 9 to 14 September, 1995. Abstracts are placed straight after that.

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

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

This also contains pointers to several other nodes: *O.K. Andersen (Stuttgart)* which includes information on the **Network Conference**, *M. Gillan (Keele)*, *B.L. Gyorffy (Bristol)*, *J. Nørskov (Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, and *A. Walker (UEA Norwich)*. If you maintain a home page on your activities we will be happy to include a pointer from the *Network's* home page to your home page.

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

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

	function
psik-coord@daresbury.ac.uk	messages to the coordinator & newsletter
psik-management@daresbury.ac.uk	messages to the NMB
psik-network@daresbury.ac.uk	messages to the whole Network

Dzidka Szotek & Walter Temmerman
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News from the Network

Concerning recent enlargement of the *Network* we have had from Brussels a contradictory information to the one published in the *Newsletter* number 8. We were told that we were not allowed to distribute *Network's* funds to the members of those additional nodes, unless formal, associated member contracts were signed. We are sorry for this confusion, which seems to have been caused by the change of rules or their ambiguous interpretation. The implications of this message may literally mean that we will not be able to fund collaborative visits of the additional nodes. However, we hope that all it tells us is that the *Network's* funds must stay in Daresbury Laboratory. Until further clarification to this point is provided we may have to subsidise such visits with greater caution if at all.

The Magnetism Working Group, V.b, of our *Network* has recently applied to Brussels for funding within Framework IV to subsidise six projects and seven postdoc positions for a period of four years. However, independently of the outcome of this application, this Working Group will remain to be part of our *Network* and will continue to participate in all *Network's* activities.

Following the example of the Magnetism Working Group of our *Network*, the *Network* as a whole is considering to submit at the next call a proposal to Brussels for funding its present activities within the Framework IV. This time apart from funding for the networking activities the intention is to seek funds for several projects and postdoc positions. This application will not exclude attempts of obtaining funds also from other sources.

News from the Working Groups

Report on the collaborative visit of A.I. Liechtenstein (Stuttgart) to Materials Modeling Laboratory, Oxford University (England)

19-23 June 1995

I discussed with Alex Bratkovsky the computational aspects of the different tight-binding model (e.g. bond-order) to the problem of dynamical calculations for transition metals and their compounds. We also analysed the computations of magnetic properties. The advantage of the real-space recursion Green-function method is the possibility of fast and accurate investigations of magnetic interactions in metals and metallic multilayers using the theory of exchange interactions described in "Magnetism and electronic structure of crystals" Springer-Verlag N-98, 1992. Another problem is related to the electronic structure of the materials with the localized d- or f- electrons. Dr. Nguyen Mahn (Oxford) pointed out the difficulties with the computations of the band structure and magnetic properties of UO_2 compound in the LDA approach. This could be overcome in the "correlated" LDA+U scheme and we agreed to collaborate on this project.

(A.I. Liechtenstein)

Report on visit by H.M. Polatoglou (Thessaloniki) to Stuttgart, 24-26 May 1995

The purpose was to visit M.W. Finnis and the group in Stuttgart and to discuss:

- Simplified models for metal-ceramic interfaces, based on tight-binding
- Monte-Carlo calculations for grain boundaries in intermetallics.

Total cost: 220 Ecu.

(H.M. Polatoglou)

Report on the collaborative visit of Ming Deng (Munich) to Daresbury Laboratory (England)

June 17-30, 1995

Recently, I made a collaborative visit to Daresbury Laboratory to do some MOKE calculations with Dr. G.Y. Guo using the Munich-Daresbury-SPRLMTO-code.

First I did calculations for the transition metals Fe, Co and Ni as simple examples for studying the influences of both l_{max} and number of the k-points on the calculation of the joint density of the states. Then I investigated the effects of both the high energy cut-off and the interval of the energy grid used for the Kramer-Kronig transformation on the calculated MOKE spectra. I found that only the well converged Kerr angles, calculated with sufficiently high energy cut-off and dense energy grid, were in good agreement with the data reported in literature (e.g., Guo and Ebert, 1994 & 1995).

Some transition metal compounds were also investigated. Especially, model calculations were carried out on Fe-Pt system with the new scheme developed in Munich for manipulating the spin-orbit coupling, which was recently implemented in the SPRLMTO code by G.Y. Guo at Daresbury Laboratory. These model calculations can provide some insight into the role of the site-dependent spin-orbit coupling for the Kerr-effect.

Finally, together with G.Y. Guo, we designed and analysed some structure models for the disordered lattice $Fe_{50}Pt_{50}$, in order to study the influence of disorder on the optical properties of this compound. The MOKE calculations for these model structures will be carried out in Munich.

No doubt, my stay at Daresbury Laboratory was very useful and it helped me to solve many problems that I had. I am very grateful to the HCM-PSIK Network for funding this collaborative visit.

(Ming Deng)

**Report on the Collaborative Visit of Michael Rohlfing
(Münster) to the group of Dr. Rex Godby
(Cambridge), 24 June – 10 July 1995**

The treatment of electronic exchange and correlation effects in terms of the GW approximation for the self-energy operator plays an important role within the investigation of solids from first principles. One important purpose of the visit was the exchange of experience on this field. In Münster, the main interest is concentrated on the understanding of the electronic band structures of complex systems, such as semiconductor surfaces and II-VI semiconductors.

We discussed the applicability of the GWA to more complicated systems and the possibility of improvements beyond the GWA.

A main topic of discussion was the understanding of localized excitations and their treatment. Usually the Green's function G of the system is constructed using wave functions and energies arising from an one-particle description of effectively non-interacting electrons, as given, for example, by density-functional theory (DFT). Such wave functions describe delocalized electronic excitations that are extended over the complete system, causing only infinitesimally small change of charge density at each atom. If spatially limited systems or localized core excitations are to be treated, this is no longer justified. We discussed possibilities of a more appropriate approach. General properties could be studied in model systems, as given, e.g., by the Hubbard model.

My expenses were:

flight Muenster-London: 318,- DM

train London-Cambridge + Taxi: 50,- Pound

accomodation: 103,- Pound

subsistance (20 ECU/day): 320,- ECU

(Michael Rohlfing)

**Report on the collaborative visit of Dr. A. Svane
(Aarhus) to Daresbury Laboratory (UK)
25 June - 15 July 1995**

W. Temmerman and Z. Szotek from Daresbury, H. Winter from Karlsruhe and A. Svane from Aarhus spent 3 fruitful weeks discussing various technical aspects of their different implementations of self-interaction corrections (SIC) within the local-spin density (LSD) approximation and exchanged bits of programs. The questions on how semi-core states are best treated within the linear-muffin-tin orbital (LMTO) method and how photoemission spectra may be calculated from SIC-LSD bandstructures were investigated.

The visit initiated a project on the computation of the electronic structure of the cerium pnictides with the SIC-LSD approach. The aim is to understand the magnetic and semi-metallic properties of these materials as well as the isostructural phase transition observed in CeP under pressure, including the question why a similar transition does not occur in CeAs and CeSb.

(Axel Svane)

Report on the Collaborative Visit of Hermann Winter (Karlsruhe) to Daresbury Laboratory (UK), 23 June - 7 July, 1995

The purpose of this visit was to further develop the LMTO-SIC method, devised in collaboration with Dr. Z. Szotek and Dr. W.M. Temmerman, for treating narrow-band electron systems. The simultaneous visit of Dr. Axel Svane from Aarhus provided the opportunity to exchange conceptual and numerical details concerning our different implementations of the self-interaction correction within the LDA, based, respectively, on the unified Hamiltonian and the Lagrange multipliers scheme, with the steepest descent minimisation technique.

We chose to study Ce-compounds, and in particular, CeSb, CeAs and CeP. Similarly to Ce, only CeP, crystallizing in the rocksalt structure, under pressure undergoes an isostructural transition from an antiferromagnetic (AFI, (001)-ordered) to a paramagnetic phase. This transition is accompanied by a 3% volume collapse. Accordingly, we discussed possibilities to better describe the 5p semi-core electrons of Ce to improve the theoretical lattice parameters for the α -phases for both Ce and its compounds. We made some improvements in this direction by applying the self-interaction corrected scheme. The work on this project continues.

In summary, this visit to Daresbury Laboratory was very profitable and I would like to acknowledge the financial support of the HCM-PSIK Network.

(Hermann Winter)

Report on a Collaborative Visit of M. Lüders (Würzburg) to Vienna, 26 June - 16 July, 1995

From 26 June to 16 July I was in Vienna to work with the group of K.Schwarz.

The purpose of the visit was to examine the possibility to incorporate the method of the optimized effective potential (OEP) into the LAPW bandstructure program.

The OEP method searches for the best *local* potential, whose orbitals minimize the total energy. Here the energy-functional, in contrast to the ordinary Kohn-Sham (KS) DFT, is a functional of the KS orbitals. Hence the exchange energy can be represented exactly. Due to the excellent results of the OPM for atoms (implemented in Würzburg using the KLI approximation and the correlation-energy functional by Colle and Salvetti) and the fact, that the OEP method is selfinteraction free it seems promising to use it also in solid-state calculations.

During my visit I reported briefly on the OEP method, on the approximation by Krieger, Li and Iafrate (KLI) and on possibilities to implement either the full OEP or the KLI.

The implementation of the full OEP seems to be ruled out by the requirement to solve the 3-dimensional integral equation. The coding of the KLI, on the other hand, seems to be straightforward since, at the beginning, existing parts of WIEN95 just need to be slightly modified. It is still an open question, whether this method can be applied to larger systems, since the computational effort might be a severe problem.

We started to build a first version of an OPM-LAPW program which should be applied to small systems in order to see whether it will be practicable.

(M. Lüders)

Announcement

Ph. D. Position

*Max-Planck Research Group “Electron Systems”, Dresden,
Germany*

A Ph. D. position is available within the field of theoretical computational solid state physics, on the subject of “Band-structure theory and *ab initio* investigation of transport properties of actinide intermetallics”. Knowledge of theoretical computational physics and experience in working with computers are required.

Starting time: as soon as possible.

Salary: about 1500–1600 DM (after tax) (BAT IIA/2-O).

Contact:

Prof. Dr. H. Eschrig

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Max-Planck Research Group
“Theory Complex and Correlated Electron Systems”
University of Technology
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Announcement

POSTDOC IN AB-INITIO SIMULATIONS OF ALUMINO-SILICATES

Oxford University Department of Earth Sciences

We are seeking to fill a position for a postdoctoral research assistant to work on Earth materials science problems involving alumino-silicate and oxide minerals. The work will use total energy pseudopotential methods and will form part of a program of study of order/disorder and water/mineral interaction processes, though there will be some flexibility regarding the specific problems to be tackled. The Earth Sciences department has substantial local computing equipment, although some parts of the work may require the use of national supercomputing facilities.

The exact duration will depend on which salary point the appointment is made at and therefore on the age and experience of the candidate, but will be approximately 16 months. The post will begin at a date in the near future by arrangement.

Candidates must have a sound theoretical background and a PhD in a relevant discipline. Experience with electronic structure calculations will be an advantage. To apply, please send your CV and letter of application to:

Professor J. D. C. McConnell
Department of Earth Sciences
Parks Road
Oxford OX1 3PR

or by email (PostScript or LaTeX are acceptable but PLEASE make sure the document is portable!) to me: "Keith.Refson@earth.ox.ac.uk".

Announcement

Ph. D. Position

University of Sheffield (UK)

A Ph. D. studentship is available from October 1995 to work with Professor Gillian Gehring (University of Sheffield) and Dr. Walter Temmerman (Daresbury Laboratory) on the total energy and Fermi surface studies of the heavy fermion compounds.

A prospective student will be expected to make a detailed study of UBe_{13} . This is expected to help the interpretation of the planned de Haas van Alphen experiments in Professor Mike Springford's group (University of Bristol). The theoretical study will involve both development or generalisation of computer codes and necessary calculations.

To apply, please send your CV and letter of application to the addresses below either by normal or electronic (only postscript or latex files are acceptable) mail.

Further information can be obtained from:

Dr. W.M. Temmerman,
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EUROPEAN RESEARCH CONFERENCES

RESEARCH CONFERENCES ON ELECTRONIC STRUCTURE OF SOLIDS: **Itinerant Magnetism**

Lunteren, The Netherlands, 9-14 September 1995

*(Co-sponsored by the European Science Foundation and The Euroconferences Activity of
the European Union)*

Chairman: Professor Balazs L. Gyorffy (Bristol),

Vice-chairman: Dr. Peter Blöchl (Zürich)

Conference Programme

Saturday, September 9 *Registration: hotel reception and
conference secretariat*

19.30 Supper

21.00 Get Together

Drinks

Sunday, September 10

MAGNETIC MULTILAYERS AND NANOSTRUCTURES

- 08.30-09.00 Opening remarks: B.L. Gyorffy (Conference Chairman), ESF and CEC representatives
- 09.00-09.40 Professor B. Johansson (Uppsala)
"Spin-Polarised Density Functional Theory"
- 09.40-10.00 Discussion lead by: Dr. P.M. Marcus (Yorktown Heights)
- 10.00-10.40 Professor P.H. Dederichs (Jülich)
"Oscillatory Coupling Between Magnetic Layers Separated By Non-Magnetic Spacers"
- 10.40-11.00 Discussion lead by: Professor B.L. Gyorffy (Bristol)
- 11.00-11.20 Coffee
- 11.30-12.10 Professor J. Mathon (London)
"Quantum Wells OF Magnetic Multilayers"
- 12.10-12.30 Discussion lead by: Dr. J. Kudrnovsky (Prague and Wien)
- 13.00 Lunch
- 16.30 Coffee
- 17.00-17.40 Professor I. Mertig (Dresden)
"Giant Magnetoresistance In Magnetic Multilayers"
- 17.40-18.00 Discussion lead by: Dr. P. Kelly (Eindhoven)
- 18.00-18.40 Professor F. Gautier (Strasbourg)
- 17.40-18.00 Discussion lead by: Professor J. Mathon (London)
- 19.15 Dinner
- 20.30-21.30 Round Table Discussion on Giant Magnetoresistance

Monday, September 11

LSDA AND BEYOND

- 09.00-09.40 Professor Peter Fulde (Dresden)
"Electronic Correlations In Cluster Calculations"
Discussion lead by: Professor B. Johansson (Uppsala)
- 10.00-10.40 Professor Ferdi Aryasetiawan (Lund)
"The GW Approximation For Transition Metal Oxides"
Discussion lead by: Professor F. Manghi (Modena)
- 11.30-12.10 Dr. Walter Temmerman (Daresbury)
"Self Interaction Corrections: Beyond LSDA"
Discussion lead by: Professor A.M. Oleś (Krakow)
- 13.00 Lunch
16.30 Coffee
- 17.00-17.40 Professor Hans Skriver (Lyngby)
"First Principles Calculations Of Magnetism Of Surfaces
And Interfaces"
Discussion lead by: Professor J. Hafner (Wien)
- 18.00-18.40 Professor Manfred Fähnle (Stuttgart)
"Magnetism In The Rare Earth Intermetallic Compounds"
Discussion lead by: Dr. M.S.S. Brooks (Karlsruhe)
- 19.15 Dinner
- 20.30-21.30 Poster Session

Tuesday, September 12

MAGNETIC ANISOTROPY

- 09.00-09.40 Dr. Stefan Blügel (Jülich)
"Spin Density Functional Theory Of Surface Magnetism"
Discussion lead by: Professor H. Skriver (Lyngby)
- 10.00-10.40 Professor Hubert Ebert (München)
"X-Ray Circular Dichroism"
Discussion lead by: Dr. P.J. Durham (Daresbury)
- 11.30-12.10 Dr. Laszlo Szunyogh (Budapest)
"The Origin Of The Magnetic Surface Anisotropy"
Discussion lead by: Professor P.H. Dederichs (Jülich)
- 13.00 Departure for excursion with packed lunches
- 17.00-17.40 Dr. Leonid H. Sandratskii (Ekaterinburg and Darmstadt)
"Non-Colinear Magnetism In Metals"
Discussion lead by: Professor H. Ebert (München)
- 18.00-18.40 Professor P.-A. Lindgård (Risø)
"Nuclear Magnetic Order In Metals"
Discussion lead by: Professor B.N. Harmon (Ames)
- 19.15 Conference Dinner
- 20.30-21.30 Poster Session

Wednesday, September 13

MAGNETISM IN DISORDERED SYSTEMS

- 09.00-09.40 Dr. J.B. Staunton (Warwick)
"Metallic Magnetism In Random Alloys"
Discussion lead by: Dr. G.M. Stocks (Oak Ridge)
- 10.00-10.40 Professor J. Hafner (Wien)
"Non-Colinear Magnetism In Amorphous Metals"
Discussion lead by: Professor J. Kübler (Darmstadt)
- 11.00-11.30 Coffee
- 11.30-12.10 Professor P. Entel (Duisburg)
"INVAR: Basic Facts, New Results And Open Questions"
Discussion lead by: Dr. P. Mohn (Wien)
- 13.00 Lunch
- 16.30 Coffee
- 17.00-17.40 Dr. J. Kudrnovsky (Prague and Wien)
"A Method For Random Surfaces And Interfaces"
Discussion lead by: Professor F. Gautier (Strasbourg)
- 18.00-18.40 Professor R.A. de Groot (Nijmegen)
"Half-Metallic Magnetism"
Discussion lead by: Professor M. Fähnle (Stuttgart)
- 19.15 Dinner
- 20.30-21.30 Poster Session

Thursday, September 14

MODEL HAMILTONIANS FROM LDA

- 09.00-09.40 Dr. W.E. Pickett (Washington DC)
"Metallic Magnetism In Random Alloys"
Discussion lead by: Professor P. Fulde (Dresden)
- 10.00-10.40 Professor A.M. Oleś (Krakow)
"Electron Correlations"
Discussion lead by: Dr. D.G. Stollhoff (Stuttgart)
- 11.00-11.30 Coffee
- 11.30-12.10 Dr. J.F. Annett (Bristol)
"Constrained Density Functional Calculations"
Discussion lead by: Dr. A.I. Liechtenstein (Stuttgart)

Calculated magneto-optical Kerr spectra of XPt_3 compounds ($\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$)

P.M. Oppeneer, V.N. Antonov^a, T. Kraft, H. Eschrig,
*Max-Planck Arbeitsgruppe "Theorie komplexer und korrelierter
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Ukraine*

Abstract

Magneto-optical spectra are calculated for the ferromagnetic state of the XPt_3 compounds (with $\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$) in the AuCu_3 structure, using density-functional band-structure theory. Large polar Kerr effects are predicted for several of these compounds, with – for a moderate spectral broadening of 0.4 eV – maximum Kerr rotations of -1.5° for MnPt_3 , and -1.0° , -1.1° for CoPt_3 , and FePt_3 , respectively. The Kerr spectra of VPt_3 , CrPt_3 , and MnPt_3 with (001) magnetization are found to be very similar in shape, as are also those of FePt_3 and CoPt_3 . The origin of the large Kerr effect in the XPt_3 alloys is shown to be caused by the spin-orbit coupling strength of Pt. A small magnetic moment on the 3d atom suffices in these materials to create already an appreciable Kerr effect. The influence of the optical transition matrix elements, magnetic moments, and spin-orbit coupling strength on each of the constituent atoms are furthermore analyzed. The orientation dependence of the polar Kerr spectra of some of the XPt_3 compounds are investigated by calculating in addition the polar Kerr spectra of some compounds in the (111) magnetization orientation. The Kerr spectra of the (111) magnetization are found to be practically identical to that of the (001) magnetization.

(submitted to Phys. Rev. B)

Manuscripts available from: peter@tmpps08.mpg.tu-dresden.de

On the Gap Anisotropy in the Layered High Temperature Superconductors

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Postfach 80 06 65, D-70506 Stuttgart, FRG

Abstract

We present a new strategy for constructing a model which deals with the normal and superconducting states on equal footing. This model reproduces very well some of the more striking features of the high-resolution photoemission experiments on the layered high T_c superconductors.

(submitted to Phys. Rev. Lett.)

Revtex file can be obtained from: w.m.temmerman@dl.ac.uk

This work has benefited from collaborations within the European Union's Human Capital Mobility Network on "Ab-initio (from electronic structure) calculation of complex processes in materials" (contract: ERBCHRXCT930369).

An order- N multiple scattering approach to electronic structure calculations

Yang Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson
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Z. Szotek, W. M. Temmerman
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Abstract

A new approach to the calculation of the electronic structure of large systems within the local density approximation is outlined. The electronic structure problem is formulated using real space multiple scattering theory. Employing a *compute node* \Leftrightarrow *atom* equivalence the method has been implemented on a massively parallel processing supercomputer. The method is naturally highly parallel and ideal order N scaling is obtained. The convergence of the method is demonstrated by comparison with the result of conventional electronic structure calculation for elemental metals and through calculation of the ordering energy of β brass.

(submitted to Phys. Rev. Lett.)

RevTeX file can be obtained from: wangy@gmsds.ms.ornl.gov

A Theoretical Study of Poly-squaraines

G. Brocks and A. Tol

Philips Research Laboratories,

Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

Most semiconducting polymers have wide band gaps in the range eV. This creates problems in doping the materials *n*-type and *p*-type and in injecting metal contacts. Most semiconducting polymers are derived from monomers which absorb in the UV. The absorption of the polymers is redshifted with respect to the monomers by band formation. In order to create a small band gap polymer it makes sense to start from monomers which absorb at long wave lengths such as there are found among dye molecules. One possible route to such polymers starting from squaraine and croconaine dyes has recently been introduced by Havinga et al¹.

In this paper we have systematically investigated a series of squaraine polymers using *ab initio* calculations and we have identified the factors which lead to a small band gap. Our principal tool is the *ab initio* CarParrinello technique for simultaneously optimizing both the electronic and the geometrical structure of the polymer. The calculated band gaps of squaraine polymers range from down to eV. A simplified Hückel analysis of the calculated π bands around the band gap reveals that the polymers separate into two classes on account of their chemical topologies. The analysis starts with the frontier orbitals of the individual chemical fragments from which the polymer is constructed. It shows that the band gap of the squaraine polymers which have been synthesized up till now reflects the HOMO-LUMO energy difference of the corresponding squaraine molecule. Band formation in the polymer shifts the energy of both the HOMO and LUMO up by similar amounts. Using the same chemical fragments as building blocks we predict that a different topology leads to polymers with much smaller band gaps. The main reason for this is that hybridization in the polymer results in an upward shift of the highest occupied level as compared to the HOMO of the squaraine molecule as before but now the lowest unoccupied state of the polymer is pinned at the position of the molecular LUMO by symmetry.

(accepted to *Synth. Met.*)

Manuscripts available from: brocks@prl.philips.nl

¹Havinga, E. E.; ten Hoeve, W.; Wijnberg, H.; *Synth. Met.* **1993**, 55-57, 299.

Full-potential photoemission calculations for the Si(100)-surface

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Abstract

In this contribution we have calculated angledependent photoelectron spectra from the Si surface along the $\Gamma X W K$ bulk mirror plane by excitation with unpolarized HeI radiation. For this theoretical investigation the fullpotential photoemission theory has been used which is a straightforward generalization of the onestep model of photoemission in the case of anisotropic spacelling cell potentials. The crystal potential employed for the determination of the theoretical data has been calculated selfconsistently within the fullpotential KorringaKohnRostoker FPKKR band structure method. The comparison with the corresponding experimental data shows a very good agreement for all bulk transitions.

(submitted to Surface Science)

Preprints available from: mgrass@nostromo.physik.Uni-Osnabrueck.de

Magnetic Anisotropy of $3d$ Transition Metal Clusters

G. M. Pastor,^{1,*} J. Dorantes-Dávila,² S. Pick³ and H. Dreyssé⁴

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Universidad Autónoma de San Luis Potosí,
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CZ-182 23 Praha 8, Czech Republic*

⁴ *Institut de Physique et Chimie des Matériaux de Strasbourg,
Université Louis Pasteur, F-67037 Strasbourg, France*

Abstract

The magnetic anisotropy energy MAE of d transitionmetal TM clusters was determined by calculating *selfconsistently* the effects of the spinorbit coupling on the spinpolarized charge distribution and on the electronic spectrum for different orientations of the magnetization. The MAE shows a complicated nonperturbative behavior as a function of cluster size, structure, bondlength and d band filling. In agreement with experiment, the MAE of small clusters is found to be considerably larger than in the corresponding crystals, often even larger than in thin films. Remarkably, the inplane anisotropy can be of the same order of magnitude as the outplane anisotropy.

(submitted to Phys. Rev. Lett.)

Manuscripts available from: hugues@lugh.u-strasbg.fr

Pressure dependence of the electrical residual resistivity of disordered alloys

John Banhart

*Fraunhofer-Institute for Applied Materials Research,
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Abstract

The pressure dependence of the electrical residual resistivity was calculated for a series of disordered AuPd alloys by using the KorringaKohnRostoker coherent potential approximation and the KuboGreenwood equation. The change of the density of states caused by an external pressure applied to the alloy is discussed and related to the change in residual resistivity. The volume coefficient of the residual resistivity is calculated from the pressure dependent resistivity and found to be in accordance with experimental findings.

(submitted to Phys. Rev. B)

Manuscripts available from: ban@ifam.fhg.de

First-principles calculation of the thermoelectric power of disordered alloys

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Abstract

The electronic structure for a series of AgPd and AuPd alloys has been calculated applying the coherent potential approximation alloy theory in connection with the KorringaKohnRostoker method of band structure calculation KKRCPA. Based on this the diffusion thermoelectric power ST of these systems has been determined making use of the KuboGreenwood equation for the dc conductivity. Very good agreement with experimental data has been achieved demonstrating the reliability of this rigorous approach. The applicability and limitations of much simpler schemes to determine ST is discussed.

(in Solid State Communications, **94**, 445, (1995))

Manuscripts available from: ban@ifam.fhg.de

Electronic structure of two-dimensional magnetic alloys: $c(2 \times 2)$ Mn on Cu(100) and Ni(100)

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Abstract

Half a monolayer of Mn deposited above K on the surfaces of Cu and Ni form ordered surface alloys of $c \times$ structure. Their electronic structure is studied in a combined experimental and theoretical work. The experimental approach combining angle-resolved photoemission and inverse photoemission characterizes both systems as ideal cases of well-ordered magnetic surface alloys and permits a complete measurement of quantum numbers. A large atom-like splitting between majority and minority Mn states is measured: ~ 1.5 eV for the Cu-based system and ~ 1.0 eV for the Ni-based system. The large splittings are direct evidence that Mn develops a high local magnetic moment in these systems. Our first-principles bandstructure calculations of $c \times$ CuMnCu and $c \times$ NiMnNi corroborate this finding and give values of $3.5 \mu_B$ and $2.5 \mu_B$ respectively for the Mn moments.

We find that the measured splittings are even larger than the ones calculated from first principles. The difference amounts to 0.5 eV and 0.2 eV for the Cu-based and Ni-based system respectively. We conclude that the splitting measured in photoemission and inverse photoemission is increased by a Coulomb energy U due to the enhanced localization of the Mn d states in the surface alloy. This high localization can be quantified by the small band dispersion of ± 0.1 meV measured for the Mn minority d band in the Cu-based system.

(submitted to Phys. Rev. B)

preprint available from: s.bluegel@kfa-juelich.de

Comment on “Structure of the Mn-induced Cu(100) $c(2 \times 2)$ surface”

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Abstract

We have studied the atomic arrangement of Mn upon deposition on Cu at room temperature using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Scanning tunneling microscopy reveals that Mn is already incorporated at very low coverages (monolayers Mn). Both LEED and STM show that the surface alloy is characterized by a considerable corrugation where Mn atoms are displaced outside by ~ 1 Å. Our findings are at variance with a recent STM study which reports a corrugation of approximately 0.5 Å and claims Mn incorporation only above a critical Mn coverage which should be larger than 0.5 monolayers.

(submitted to Phys. Rev. B)

Preprint available from: s.bluegel@kfa-juelich.de

Confinement and the CLOPW Method

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Abstract

A new mixed basis for electronic structure calculations has been constructed using a basis set consisting of localised orbitals conned CLOs to mun tin spheres and plane waves PWs. The connement suppresses smoothly the tails of atomic orbitals and eliminates hence multicenter integrals. From LMTO selfconsistent potentials the bulk electronic structures of Cu and Si have been obtained as accurate as the original LMTOtype results. The energy independent CLOPW basis functions enable full solution without using linearization schemes.

(accepted for publication by Phys. Rev. B)

Revtex manuscript can be obtained from: wijers@tn.utwente.nl

Magnetic Structures of Uranium Compounds: Effects of Relativity and Symmetry

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Abstract

We report results of calculations that explain the noncollinear magnetic structures observed in U_3P_4 and U_2Pd_2Sn in the itinerant electron picture. We use the local approximation to spin density functional theory and the ASW method incorporating spin-orbit coupling (SOC) and noncollinear moment arrangements. We show how the relativistic effect of SOC and the different symmetry properties of U_3P_4 and U_2Pd_2Sn cooperate leading in the case of U_3P_4 to ferromagnetic and in the case of U_2Pd_2Sn to antiferromagnetic noncollinear structures.

(submitted to Phys. Rev. Lett.)

Latex version can be obtained from: dg5m@mad1.fkp.physik.th-darmstadt.de

The Electronic Structure of La_2BaCuO_5 : A Magnetic Insulator

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Abstract

The results of density functional calculations of the electronic structure of La_2BaCuO_5 are presented. The calculations used the standard spin polarized Local Density Approximation. The system is found to be a strong ferromagnet and has an insulating ground state. The results of the calculations show excellent agreement with the electronic configurations, magnetic ordering and the localized magnetic moments inferred from experiments.

(accepted for publication by Europhysics Letters)

REVTeX-file can be obtained from: eyert@physik.uni-augsburg.de

Ab-initio calculation of the lattice relaxation in dilute alloys

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Abstract

We present an extension of the fullpotential KorringaKohnRostoker Green function method to treat lattice relaxation around point defects in crystalline solids. The equilibrium atomic positions in the vicinity of the defect are obtained from total energy and/or force calculations. Our results for the displacement of the first nearest neighbours in the case of d impurities in Cu are in good agreement with the available EXAFS experimental data.

(To be published in: Proceedings of the NATO-ASI "Stability of Materials",
June 25-July 7, 1995, Corfu-Greece)

Preprints available from: nstefan@atlas.uoa.ariadne-t.gr

(This paper acknowledges the support of the Network)

Excitation Energies from Time-Dependent Density-Functional Theory

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Abstract

A new densityfunctional approach to calculate the excitation spectrum of many electron systems is proposed. It is shown that the full linear density response of the interacting system which has poles at the exact excitation energies can rigorously be expressed in terms of the response function of the noninteracting Kohn-Sham system and a frequencydependent exchange-correlation kernel. Using this expression the poles of the full response function are obtained by systematic improvement upon the poles of the Kohn-Sham response function. Numerical results are presented for atomic systems.

Physical Review Letters (submitted)

Preprints available from: ptrslka@physik.uni-wuerzburg.de

GENERALIZED VARIATIONAL APPROACH TO KIM-GORDON ELECTRON GAS THEORY FOR IONIC CRYSTALS

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Abstract

The generalized approach to the KimGordon electron gas model is proposed. The total density of a crystal is considered as a superposition of densities of individual overlapping ions. The possible distortions of individual ion densities are calculated in the presence of some auxiliary external potentials. The real values of these distortions are calculated by a variational method from the minimum total energy of a crystal. The proper prescription of the ion selfenergy with a distorted density is given using the method elaborated in the nonequilibrium thermodynamics. Some examples of the calculation for phonon frequencies are presented and demonstrate a good agreement with experimental data.

(submitted to Solid State Commun.)

Manuscripts available from: maksimov@ru.ac.lpi

Light emission at room temperature from Si/CaF₂ multilayers

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Abstract

We have synthesized by Molecular Beam Epitaxy SiCaF₂ multilayers which are optically active at room temperature. The photoluminescence spectra present a blueshift for decreasing Si layer thickness in analogy to those obtained from porous silicon when the porosity is increased. We find a critical dependence of the photoluminescence efficiency on the thickness of the Si layers. Our results allow us to conclude unambiguously that quantum confinement is a necessary condition for the observation of visible luminescence in our Si-based structures. We compare the experimental results to *ab initio* calculations of the band structure of SiCaF₂ multilayers which predict the band gap opening and the presence of confined and interface states leading to a quasidirect bandgap.

(Europhysics Letters (in press))

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Hole Filling and Interlayer Coupling in $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{PrBa}_2\text{Cu}_3\text{O}_7$ Superlattices

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Abstract

Charge transfer effects in $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{PrBa}_2\text{Cu}_3\text{O}_7$ superlattices have been proposed by many authors as the origin of the experimentally observed strong depression of the critical temperature. We performed selfconsistent LMTOASA calculations and found that no remarkable change in the electronic structure of the superconducting CuO_2 planes occurs in the studied structures when the PBCO layer thickness is varied. The observed depression of the critical temperature does not seem to be originated intrinsically by a severe modification of the electronic structure or by the hole-filling mechanism.

(Europhysics Letters (in press))

Manuscripts available from: ossicini@imoax1.unimo.it

Electronic Structure of $\text{PrBa}_2\text{Cu}_3\text{O}_7$: A local-spin-density approximation with on-site Coulomb interaction calculation

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Abstract

Electronic structure calculations based on the local spin density approximation fail to reproduce the antiferromagnetic ground state of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (PBCO). We have performed LMTOASA calculations based on the local spin density approximation with on-site Coulomb correlation applied to Cu and Cu d states. We have found that inclusion of the on-site Coulomb interaction modifies qualitatively the electronic structure of PBCO with respect to the LSDA results and gives Cu spin moments in good agreement with the experimental values. The Cu upper Hubbard band lies about 1 eV above the Fermi energy, indicating a Cu^{II} oxidation state. On the other hand, the Cu upper Hubbard band is located across the Fermi level, which implies an intermediate oxidation state for the Cu ion between Cu^I and Cu^{II} . The metallic character of the CuO chains is preserved in agreement with optical reactivity [K. Takenaka *et al.* Phys. Rev. B **46**] and positron annihilation experiments [L. Homann *et al.* Phys. Rev. Lett. **71**]. These results support the view of an extrinsic origin of the insulating character of $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

(Phys. Rev. B (in press))

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Electronic structure and elastic properties of Au/Cr (001) superlattices

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Abstract

We present a first principle calculation of the electronic structure and elastic properties of a series of AuCr superlattices with modulation wavelengths between Λ and 2Λ . The electronic structure calculations are performed with the Linear Muffin-Tin Orbital method in the Atomic Sphere Approximation. Results for the density of states and the charge transfer at the interfaces as a function of the modulation wavelength are presented. The Force Theorem has been used in the investigation of the elastic behaviour of the system. We have performed a detailed analysis of the variation of the band contribution to the shear elastic constant c_{44} with particular reference to the Fermi surface contribution. This analysis allows us to investigate the role of the electronic structure variations induced by layering in the elastic anomalies experimentally observed in metallic superlattices. We show that the origin of the enhancement of the c_{44} elastic constant observed in AuCr at small modulation wavelengths cannot be ascribed to a Fermi surface Brillouin zone interaction mechanism.

(Phys. Rev. B51, 4497-4506 (1995))

Extended S-Wave and Gapless Superconductivity due to Antiferromagnetism: A Model inspired by HTS

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Abstract

We present a model of a superconductor SC in the presence of spiral or anti ferromagnetic AF order with a quasiparticle spectrum corresponding to high temperature superconductors HTS . In the case of *swave pairing* in absence of the magnetic order it is found that when the exchange energy h_{ex} is larger than the SC order parameter Δ ie $h_{ex} \geq \Delta$, the superconductivity is of the extended *s-wave* type and the quasiparticle spectrum is gapless with nodes on either side of the π, π diagonal in k space. This gives rise to power law behavior wrt to temperature and frequency of various quantities. The Knight shift the electronic Raman scattering the ultrasound attenuation and the specic heat are calculated and these quantities show characteristic features of the anisotropic gapless superconductor.

This theory might also be applicable to the heavyfermion systems like UPt_3 UBe_{13} URu_2Si_2 UPd_2Al_3 UNi_2Al_3 and to the new rareearth borocarbides $HoNi_2B_2C$

(Physica C245, 185-192)

Manuscripts available from: liechten@radix6.mpi-stuttgart.mpg.de

Electron-Boson Interaction Can Help $d - Wave$ Pairing: Self-Consistent Approach

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Abstract

We show that the critical temperature for the $d - wave$ pairing which is due to the spin fluctuations in the $D t - t'$ model can be even increased in the presence of the strongly momentum \vec{k} dependent electronboson phonon plasmonexciton etc interaction. The condition for this effect is that in comparison to the momentum independent case the electronboson coupling must be increased at $\vec{k} \approx$ and decreased for large \vec{k} . The possible mechanism for such a behavior of the coupling constant based on strong correlations is also discussed.

The problem is studied selfconsistently in the framework of the strong coupling Eliashberg equations by taking into account spin and charge fluctuations as well as the electronboson interaction.

(Physica C245, 186-192)

Manuscripts available from: liechten@radix6.mpi-stuttgart.mpg.de

The electronic structure and physical properties of NbSi_2

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Abstract

We have investigated the optical properties of NbSi_2 experimentally and theoretically. The reactivity and ellipsometry measurements were performed on single crystals with two light polarizations. From these the optical conductivity and the complex dielectric function were obtained from ~ 0 to about 10 eV. The measured optical functions were compared with those calculated using local density functional LDA theory and the linear muntin orbital LMTO method. The calculated electronic structure is analyzed using orbital projected densities of states DOS and the optical functions are interpreted in terms of interband transitions. We further more compare the calculated DOS with previously measured XPS and BIS spectra. We have nally calculated some soft Xray emission spectra and compare them with experiments. We nd generally excellent agreement between theory and all experiments.

(Phys. Rev. B, submitted)

Manuscripts available from: jepsen@radix1.mpi-stuttgart.mpg.de

Screened spherical waves and improved KKR and LMTO methods

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Abstract

Screened spherical waves defined in terms of inhomogeneous hard-sphere boundary conditions form a convenient set of functions for interpolation across the interstitial. When used for solution of the Poisson and Schrödinger equations which describe electrons in condensed matter improved Korringa-Kohn-Rostoker (KKR) and linear-muffin-tin-orbital (LMTO) methods result. The screened KKR matrix has reduced energy dependence and range. The new LMTO basis is complete to first order in energy not only inside the muffin-tin spheres but also in the interstitial. With a suitable generalization of the partial waves the formalism remains as in the atomic sphere approximation.

(Phys. Rev. Lett., submitted)

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Magnetism of 3d, 4d, and 5d transition metal impurities on Pd(001) and Pt(001) surfaces

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Abstract

We present the first systematic *ab initio* calculations for the magnetic moments of 3d, 4d and 5d transition metal impurities as single adatoms on the surfaces of Pd and Pt. Large magnetic moments are found for all d adatoms except for Sc and Ti which are nonmagnetic. Among the 3d and 4d adatoms Mo, Tc, Ru, and W, Re, Os have large magnetic moments. Also the adatom-induced magnetization of the Pd and Pt surfaces is investigated. We compare our results with the calculations for bulk systems and for monolayers on these substrates.

(submitted to Phys. Rev. B)

Latex file available from: hergert@physik.uni-halle.d400.de

This work has benefited from collaborations within the Network on "Ab initio (from electronic structure) calculation of complex processes in materials" (contract: ERB-CHRXCT930369)

Model potential for the ferroelectric ABO_3 perovskites

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Abstract

While pure $KTaO_3$ is an incipient ferroelectric which does not undergo any phase transition $KNbO_3$ undergoes a sequence of three phase transitions. Our specific goal is to clarify the validity of the nonlinear shell model to describe the totally different behavior observed in $KTaO_3$ and $KNbO_3$ by comparing the underlying static potential for different atomic distortions with recent ab initio calculations.

Presented at 8th European Meeting on Ferroelectricity (Nijmegen, 4-8/7/95).

(to appear in *Ferroelectrics*)

Manuscripts available from: migoni@ifir.edu.ar

MOLECULAR DYNAMICS SIMULATION OF
KNbO₃ :
RELAXATIONAL DYNAMICS AND PRECURSOR
DOMAINS

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Abstract

The dynamics of the ferroelectric phase transition in KNbO₃ is studied by means of a molecular dynamics simulation in the framework of the nonlinear oxygen polarizability model. The validity of the shell model potential to describe the sequence of phase transitions in KNbO₃ is tested by comparing the underlying static potential for the ferroelectric distortions with recent abinitio calculations. The specific goal is to study the crossover from displacive to order-disorder behavior near the cubic-tetragonal phase transition. The appearance of a central peak in the dynamical structure factor and the onset of relaxation in the local ionic dynamics are analyzed.

Presented at 8th European Meeting on Ferroelectricity (Nijmegen, 4-8/7/95).

(to appear in *Ferroelectrics*)

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LATTICE DYNAMICS OF THE INFINITE-LAYERED COMPOUNDS

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Abstract

We obtain for the first time the phonon dispersion relations of Press any key to return to indexes of a shell model. We start from potential parameters and polarizabilities available from fits of phonon data in several high T_c cuprates. With modification of only a few parameters we achieve a good fit of the infrared phonon data available for the narrowband semiconductor $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$. A virtual crystal approximation is made for the $\text{Ca}_{0.86}\text{Sr}_{0.14}$ ion. Comparing the parameters to those of other cuprates we observe a higher covalence degree of the CuO bond in this material. By substituting the Cu-related parameters by Nd ones we also study the changes in the phonon density of states compared to that of the superconductor $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$. $T_c \simeq \text{K}$

(submitted to Physica C (July 1995))

Manuscripts available from: migoni@ifir.edu.ar

Preprints from Center for Atomic-scale Materials Physics (CAMP)

- C. Klink, I. Stensgaard, F. Besenbacher, and E. Lægsgaard:
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Surf.Sci. submitted
- B. Hammer and J.K. Nørskov:
Electronic factors determining the reactivity of metal surfaces,
Surf.Sci. submitted
- M. Brandbyge, J. Schiøtz, M.R. Sørensen, P. Stoltze, K.W. Jacobsen, J.K. Nørskov, L. Olesen, E. Lægsgaard, I. Stensgaard, and F. Besenbacher:
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- P. Kratzer, B. Hammer, F. Grey, and J.K. Nørskov:
Stability of adsorbed hydrogen on Si(100) under changes of the surface potential,
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- M.R. Sørensen, K.W. Jacobsen, and P. Stoltze:
Simulations of atomic-scale sliding friction,
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- P. Kratzer, R. Russ, and W. Brenig:
Ab initio quantum dynamics of H₂/Si(100) adsorption/desorption on a 3D potential,
Surf.Sci. submitted
- A.C. Luntz and P. Kratzer:
D₂ dissociative adsorption on and associative desorption from Si(100): dynamic consequences of an ab-initio potential energy surface,
J.Chem.Phys. submitted

More information can be obtained from helle@fysik.dtu.dk

Presenting Other HCM Networks

Quantum Monte Carlo Calculations for Real Solids

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Solid state Quantum Monte Carlo (QMC) is a very new technique and is still in the early stages of development. Progress has been rapid, however, and the aim of this article is to summarise what has been achieved so far. I'll describe the method, discuss its strengths and weaknesses, and tell you about our work and our EC Network.

(1) What is Solid State Quantum Monte Carlo?

This section contains a simple explanation of solid state QMC. I hope it will be of interest to readers who don't know much about the subject, but experts should skip straight to section (2).

QMC [1] is a general term used to describe any method that uses random numbers and computer experiments to solve the Schrödinger equation. Sometimes the quantum particles are atoms, as in McMillan's famous work on liquid He, but they can also be interacting electrons. Chemists have been using QMC to solve the many-electron Schrödinger equation for more than 20 years, but the required computer time scales as the 5th or 6th power of the atomic number and so almost all applications have been to atoms in the first row of the periodic table. It was not until 1988 that Stephen Fahy [2] realised that QMC could be combined with norm-conserving pseudopotentials as used in plane-wave LDF calculations. This simple insight completely solved the atomic number scaling problem and it suddenly became possible to apply QMC to interesting solids. It is important to realise that pseudopotential QMC is a genuine many-body theory: the core-valence exchange-correlation effects are approximated because the pseudopotentials are derived from LDF theory, but the interactions among the valence electrons are treated explicitly and are not modelled by a one-electron exchange-correlation potential.

QMC simulations can only be carried out in finite systems and so solids must be modelled by small simulation cells subject to periodic boundary conditions. The required computer time is proportional to the cube of the number of atoms in the simulation cell, and the current practical limit is a few hundred atoms. This is large enough to give reasonably accurate results in many cases, but finite size effects are often a problem.

Although there are many different QMC methods [1], only variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) have been applied to real (pseudopotential) solids. Both these methods give ground state properties at zero temperature. Other methods, such as path integral Monte Carlo, auxiliary field Monte Carlo, and Green's function Monte Carlo, have been used to study atoms, molecules, and model systems such as Hubbard models, but will not be discussed here.

As its name suggests, VMC is based on the variational principle and relies on finding a good trial ground state wavefunction, $\Psi_T(\mathbf{R})$, where $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the $3N$ dimensional vector of electronic positions and N is the number of electrons in the simulation cell. At first sight, the chances of guessing a good trial function look slim, but a surprising number of many-body problems have been solved this way (think of BCS theory and the fractional quantum Hall effect). In weakly correlated solids a simple Slater-Jastrow function,

$$\Psi_T(\mathbf{R}) = \exp\left(\sum_{i=1}^N \chi(\mathbf{r}_i) - \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N u_{\sigma_i \sigma_j}(r_{ij})\right) \times D^\uparrow(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_{N_\uparrow}, \sigma_{N_\uparrow}) \\ \times D^\downarrow(\mathbf{r}_{N_\uparrow+1}, \sigma_{N_\uparrow+1}, \dots, \mathbf{r}_{N_\uparrow+N_\downarrow}, \sigma_{N_\uparrow+N_\downarrow}) \quad , \quad (1)$$

seems to work well, and almost all calculations for real solids have used this form. D^\uparrow and D^\downarrow are Slater determinants of spin-up and spin-down one-electron states respectively, and the $u_{\sigma_i \sigma_j}(r_{ij})$ terms suppress the wavefunction when two electrons approach each other, so building in some electronic correlation. The Slater determinants are constructed using one-electron orbitals obtained from good LDF calculations and so the density due to the determinants alone is quite accurate. A side effect of introducing the $u_{\sigma_i \sigma_j}(r_{ij})$ correlation factors is to smear out the density, and the χ functions were introduced by Fahy [2] to counteract this smearing effect.

In principle, the $u_{\sigma_i \sigma_j}$ and χ functions and the one-electron orbitals may all be adjusted to minimize the total energy, but in practice this has never been done. Instead, the one-electron wavefunctions have been obtained from LDF calculations, the $u_{\sigma_i \sigma_j}$ functions have been assumed to have some fairly arbitrary form with the correct behaviour as $r \rightarrow 0$ and $r \rightarrow \infty$, and χ has been designed to ensure that the final electron density is close to the LDF density (which may or may not be accurate). One of our most useful pieces of work [3] has been to improve this procedure. We now expand $u_{\sigma_i \sigma_j}$ and χ as Chebyshev series and find the expansion coefficients variationally by minimizing the total energy (actually we minimise the variance of the energy, but this is a technicality). This allows us to improve our variational energy estimates significantly and reduces our statistical errors by an order

of magnitude.

Even when good trial functions are known, the evaluation of expectation values is no trivial matter: our largest simulations have included 600 electrons and so expectation values are 1800 dimensional integrals. These can only be evaluated statistically using Monte Carlo integration [1]. Taking the total energy as an example, the expectation value is written in the form,

$$\langle E \rangle = \int d\mathbf{R} E_L(\mathbf{R}) \left[\frac{|\Psi_T(\mathbf{R})|^2}{\int d\mathbf{R}' |\Psi_T(\mathbf{R}')|^2} \right] , \quad (2)$$

where $E_L(\mathbf{R}) = \Psi_T(\mathbf{R})^{-1} \hat{\mathbf{H}} \Psi_T(\mathbf{R})$ is known as the local energy. The term in square brackets is interpreted as a probability distribution and the Metropolis algorithm [1] is used to generate a set of points, $\{\mathbf{R}_i ; i = 1, M\}$, distributed according to that distribution. An unbiased statistical estimate of the integral is then given by,

$$\langle E \rangle = \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i) , \quad (3)$$

and the statistical errors are proportional to $1/\sqrt{M}$ independent of the dimension.

That is really all there is to VMC. You need a good trial wavefunction which can be evaluated easily and for which the local energy can be evaluated easily, but there are no hidden subtleties. The code required is perhaps a little harder to write than a plane-wave LDF code and the calculations require much more computer time, but most of the steps (Ewald sums, evaluation of one-electron wavefunctions, ...) are very similar. The problem, of course, is that everything hinges on finding a good trial wavefunction, and there's no reason to suppose that this will be possible in strongly correlated solids. The DMC method gets around this problem to some extent, but is more difficult to implement than VMC and requires even more computer time.

DMC is a method for solving the imaginary time Schrödinger equation,

$$\left(\frac{1}{2} \nabla_{\mathbf{R}}^2 - V(\mathbf{R}) \right) \Psi(\mathbf{R}, \tau) = \frac{\partial}{\partial \tau} \Psi(\mathbf{R}, \tau) , \quad (4)$$

where $\nabla_{\mathbf{R}}^2$ is the full $3N$ dimensional Laplacian and $V(\mathbf{R})$ includes the electron-electron interactions as well as the electron-ion interactions. The phrase “in imaginary time” is catchy but confusing: the ordinary Schrödinger equation certainly turns into Eq. (4) if you set $\tau = it$, but τ is a real variable as far as we are concerned so it's best to forget about this. The point about the imaginary time Schrödinger equation is that any starting state, $\Psi(\mathbf{R}, \tau = 0)$, which has a non-zero overlap with the ground state, tends to the ground state as $\tau \rightarrow \infty$. (To see this, expand $\Psi(\mathbf{R}, \tau = 0)$ as a linear combination of energy eigenfunctions and consider how each eigenfunction develops in imaginary time.) If we could follow the imaginary time development of the starting state, we would therefore have a way of finding the ground state.

The other nice thing about the imaginary time Schrödinger equation is that it looks like a diffusion equation for particles in $3N$ dimensional configuration space. These particles

are often called walkers or configurations and are not the individual electrons (each walker contains information about the positions of *all* the electrons in the simulation cell). The $V(\mathbf{R})$ term causes the walkers to multiply or die out as they diffuse around, but the physics is easy to understand and easy to model on a computer. We can therefore solve the imaginary time Schrödinger equation by carrying out a computer simulation of a $3N$ dimensional diffusion/replication/death process. The procedure is to start with a population of a few hundred walkers, choose a small imaginary time step, $\Delta\tau$, and start moving the walkers around step by step according to Eq. (4). As they diffuse, some of the walkers will multiply and others will die out, but the total population can be kept roughly constant by choosing the zero of energy appropriately. Eventually, the simulation settles down and the walkers start to sample the ground state wavefunction in the same probabilistic sense that the configurations \mathbf{R}_i sampled the distribution $|\Psi(\mathbf{R})|^2$ in VMC. The accumulation of ground state expectation values is then fairly straightforward.

There is an obvious objection to the DMC algorithm just described, which is that the ground state wavefunction of a fermionic system must be totally antisymmetric and so cannot be positive everywhere; the ground state cannot be interpreted as a probability distribution and cannot be sampled by the diffusing walkers. In fact, the algorithm described above gives the boson ground state, which is everywhere positive and has a much lower energy than the fermion ground state. This is the infamous sign problem, which plagues all fermion QMC methods. Various supposedly exact solutions to this problem have been proposed, most of which involve introducing both positive and negative walkers, but all suffer from errors that diverge exponentially as τ increases.

The only numerically stable solution to the sign problem is an approximation called the fixed node approximation. The starting point is a good guess at the $3N - 1$ dimensional nodal surface (the surface of zeros) of the many-electron ground state wavefunction. In practice, this means choosing a trial function — probably obtained from an earlier VMC calculation — and using its nodal surface as the guess. The imaginary time Schrödinger equation is then solved independently in each nodal pocket (each region enclosed by a piece of nodal surface), with the boundary condition that the solution must vanish on the surrounding nodal surface. This sounds impossibly difficult, but in fact it's easy to implement: the walkers diffuse, multiply and die as normal, but walkers that cross nodes are deleted. Node crossing moves are easily identified by checking to see whether the sign of the trial function changes.

It can be shown that the energy obtained using this procedure is always greater than or equal to the exact ground state energy, and that it tends quadratically to the exact energy as the trial nodal surface tends to the exact ground state nodal surface. The fixed node DMC method is thus a natural improvement on the VMC method: VMC gives the energy of a particular trial function, whereas DMC gives the lowest possible energy consistent with the nodal surface of that trial function. Fixed node DMC has been widely used in atomic and molecular calculations and is usually very accurate, with typical errors of just

a few percent of the correlation energy. A few calculations have also been carried out in solids (Si, Ge, N, H) and the agreement with experimental results has been impressive: there is no more accurate method for calculating total energies in weakly correlated solids.

There's one more problem with the DMC algorithm described above. $V(\mathbf{R})$ blows up when two electrons approach each other or when one electron is very close to a nucleus, and this leads to wild fluctuations in the total walker population and very large statistical errors. The solution is to make an "importance sampling" transformation. The imaginary time Schrödinger equation is rearranged to describe the development of the function $f(\mathbf{R}, \tau) = \Psi_T(\mathbf{R})\Psi(\mathbf{R}, \tau)$, where $\Psi_T(\mathbf{R})$ is the same time-independent trial function used to determine the nodal surface. The equation of motion for $f(\mathbf{R}, \tau)$ looks very like Eq. (4) but differs from it in two important ways: the wildly fluctuating potential, $V(\mathbf{R})$, is replaced by the much smoother local energy, $E_L(\mathbf{R})$ (which is a constant if the trial function is the exact ground state); and a new drift term appears so that, as well as diffusing, the walkers also drift with a position-dependent velocity. The fact that the walkers now sample $f(\mathbf{R}, \tau)$ instead of $\Psi(\mathbf{R}, \tau)$ changes the implementation of the fixed node approximation (moves that attempt to cross nodes should be rejected without deleting walkers), but the simulation is still quite straightforward and the statistical errors are much decreased.

(2) Achievements and Limitations of Quantum Monte Carlo

Before asking how QMC compares with other approaches, it is useful to summarise the achievements and current limitations of the method. The first thing to admit is that QMC has only been applied to a few solids and all of them (Si, Ge, C, N, H) have been quite weakly correlated. LDF theory works well in such solids and so the QMC calculations have not told us anything new, except perhaps that simple Slater-Jastrow wavefunctions work surprisingly well. The one significant success has been in the evaluation of cohesive energies: our QMC calculations for Ge gave a cohesive energy within $0.1eV$ of the experimental value, whereas LDF calculations overestimate the cohesive energy by about $0.75eV$. The $0.1eV$ accuracy of the QMC result is not atypical, and QMC calculations have given better cohesive energies than LDF calculations in all cases investigated so far.

The main errors in QMC calculations are the "physical" errors caused by the inadequacies of the trial function in VMC and by the fixed node approximation in DMC. Poor trial functions lead to poor VMC energies and large variances. The variance can be decreased (slowly) by running the simulation for longer, but a better approach is to optimise the trial wavefunction, which simultaneously reduces the variance and lowers the variational energy estimate. We have been among the first groups to make a serious attempt at this [3] (Stephen Fahy has also been working on it), and now optimise both our χ and $u_{\sigma_i\sigma_j}$ functions extensively. This won't be much help in cases where the Slater-Jastrow form of wavefunction is physically wrong, but it does work well for the weakly correlated solids we have been studying. For Si and Ge we can now reduce the statistical errors in the average energy to less than $0.01eV$ per atom with a reasonable expenditure of computer

time. We can also decrease the difference between the VMC and DMC energies (a measure of the difference between the trial wavefunction and the best obtainable wavefunction with the given nodal surface) to less than $0.3eV$ per atom, much of which can be attributed to the finite energy cut-off in the plane-wave LDF calculations used to generate the one-electron orbitals for the Slater determinants.

The next most important errors in QMC calculations are finite size errors. On current workstations and vector supercomputers it is taxing to study simulation cells containing more than 100 atoms, but the finite size errors for such systems may be more than $0.2eV$ per atom even after the application of corrections derived from LDF or Hartree-Fock calculations. Larger systems can be studied on massively parallel machines, but the finite size errors decrease very slowly ($\sim 1/N$) with system size. Fortunately, we have recently made two separate advances in our understanding of these errors and have been able to reduce them by almost an order of magnitude [3]. The first advance was the introduction into QMC calculations of the analogue of the special k -point sampling methods used in LDF calculations; and the second was a new understanding of the slowly decaying $1/N$ residual errors. We were not surprised when we found that the $1/N$ errors are Coulomb effects, but did not expect to discover that they can be entirely removed by changing the form of the simulation cell Hamiltonian (we are sure about this for jellium, and preliminary results for real solids also look good). The new simulation cell Hamiltonian does not involve any Ewald sums and is much quicker to evaluate than the standard Hamiltonian. The resulting QMC algorithm has much smaller finite size effects than the traditional approach, and runs significantly faster (more than 20 times faster for jellium).

To summarise the last two paragraphs, the message is that both the wavefunction errors and the finite size errors add up to less than $0.1eV$ per atom for weakly correlated solids and reasonable system sizes. The only error we are unable to check easily is the error due to the fixed node approximation, but this is small for atoms and molecules and we hope it will be small for solids as well.

The achievements of QMC to date are unimpressive because it has only been used to tackle weakly correlated solids that are well described by LDF theory. The last few years have seen significant technical improvements, but QMC will not become interesting until it can be used to look at strongly correlated systems. Why hasn't this been done already? One of the main problems has been pseudopotentials: there are technical difficulties associated with the use of non-local pseudopotentials in DMC which are still not solved (partial solutions have existed for some years, but none is wholly satisfactory). The good news is that there are some new and promising ideas around at the moment (not our ideas, unfortunately) and I am hopeful that the problem will be solved within the next year or two.

Unlike DMC, VMC works fine with non-local pseudopotentials and so there is no reason not to try it for some strongly correlated solids. The main obstacle will be the enormous amounts of computer time required, but the recent advances in trial function optimisation

should alleviate this problem to some extent. The project is risky because there is no way to know whether it will be possible to guess an adequate trial wavefunction, but I am sure that VMC will be applied to transition metals and transition metal oxides within the next few years. Then, and only then, will we know whether all this work has been worthwhile.

(3) Strengths and Weaknesses of Quantum Monte Carlo

The greatest strength of QMC is that it is variational rather than perturbative. It is therefore possible (although this has not yet been demonstrated) that QMC will be useful in strongly correlated solids where perturbative approaches such as GW are no good. I am wary of saying that QMC is the *only* non-perturbative many-electron method that has been used successfully in real solids, but it is hard to think of another. Some QMC methods generalise straightforwardly to finite temperature, and the (distant) prospect of studying the finite temperature properties of real strongly correlated solids is also very enticing.

The relatively innocuous N^3 system size scaling is another great strength of QMC. The scaling is no worse than in a standard LDF calculation, and vastly much better than the exponential scaling in a CI calculation. Furthermore, QMC calculations are almost trivially parallel and so can take full advantage of the power of massively parallel computers. In our VMC work on the Cray T3D we put one walker on each node and let each processor do a separate VMC run. No communication between nodes is necessary, and the number of configurations we can generate per second increases linearly with the number of nodes we use (up to the maximum 256 nodes). Our DMC calculations do require some inter-processor communication, but the amount is negligible and we still achieve linear scaling.

The main weakness of QMC is that it is a ground state method, whereas most of the interesting properties of correlated systems concern the excitations. This is a fundamental drawback, and one which is unlikely to be solved. Another commonly raised criticism is that QMC results are not a theory; it is quite possible to get results that agree with experiment without learning anything about the underlying physics. I don't look at it this way, however, and prefer to regard QMC as a special sort of experimental technique. It may generate types of "experimental" data that could not be obtained otherwise, but no more should be expected of it than of any other experimental method. A good QMC calculation is simply one that produces correct and interesting data; the use you make of that data is a separate matter.

The other main ground state method is LDF theory. It would be nice to compare the QMC and LDF approaches in strongly correlated solids, of course, but this is impossible because no QMC calculations have been done for such systems. In weakly correlated solids the LDF results are usually very accurate, but QMC does have the significant advantage that it can be used to calculate two-electron properties such as pair correlation functions that are not accessible in LDF theory. Most of the other drawbacks of the LDF approach in weakly correlated solids are minor, the worst being the overestimation of the cohesive energy and

the underestimation of the band gap. We have already said that QMC calculations give good cohesive energies, and we are currently involved in a calculation of the band gap of Si (obtained from the ground state energies of the $N - 1$, N , and $N + 1$ electron systems) to see whether QMC also cures the band gap problem. At the moment it is too early to say (the finite size errors are causing problems), but we are reasonably optimistic.

The GW method is principally for calculating excitation properties and so is not directly comparable with QMC. Hartree-Fock calculations use an optimised determinantal trial function but no Jastrow factor, and are much inferior to VMC calculations using a Slater-Jastrow trial function.

This section may be summed up in two sentences. QMC cannot compete with LDF theory in weakly correlated systems except in a few special cases. The long term future of QMC therefore rests on how well it performs in more strongly correlated systems, and this is still an open question.

(4) The European Community QMC Network.

The “home” of QMC is David Ceperley’s group at the University of Illinois, which has been responsible for many of the major developments over the years. With the recent advent of solid state QMC, however, a considerable European effort has developed. The European Community Human Capital and Mobility Research Network on Solid State QMC is coordinated by Stephen Fahy of University College, Cork, and comprises 7 groups in 6 countries. It is much smaller than the Ψ_k leviathan and also must poorer, but the amount of funding received was enough to pay one post-doc for two years (he is Maziar Nekovee and has just started work at Imperial College) and to allow a generous amount of travel. The network only came into operation last Christmas (two years after submitting the proposal!) and many of the collaborations suggested in the proposal were already in operation by then, but the travel money will no doubt help them to prosper. As far as I know, there are only three solid state QMC codes in existence: one comes from Illinois, one was written by Stephen Fahy, and one was written by the Cambridge/Imperial College group (mostly by Guna Rajagopal). Two out of the three are connected with the EC QMC Network.

(5) Current Work.

I have not had room in this article to describe most of the QMC work at Cambridge and Imperial College, so I thought I’d finish by listing the various projects and asking you to get in touch if you would like more information. This is a list of the work that has been published or submitted for publication [3]:

- Optimised Ewald sums;
- Total energy calculations for diamond structure Germanium;

- Special k -point sampling in QMC;
- Relativistic QMC calculations for atoms;
- Finite size effects in QMC calculations for homogeneous systems with periodic boundary conditions;
- Variance minimisation and wavefunction optimisation for QMC;

and these are the projects now underway:

- The band gap of Silicon;
- Positron annihilation in solids;
- Calculating exact exchange-correlation potentials using QMC;
- Relativistic QMC calculations for jellium;
- Finite size effects in QMC calculations for real solids.

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HIGHLIGHT OF THE MONTH

Mixed-stack organic charge-transfer compounds

(A few steps in the jungle)

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1 Introduction

Charge-transfer (CT) molecular compounds are composed of two types of nearly flat organic molecules: closed-shell- π -electron donors (D) and acceptors (A). In the crystalline state, the tendency for these molecules is to pile up along linear and often parallel chains, like hands put one above the other one, thus forming either segregated stacks: $\dots D - D - D - D \dots$ and $\dots A - A - A - A \dots$, or mixed-stacks: $\dots D - A - D - A \dots$. The electron transfer from D to A is at the origin of the very interesting electronic, magnetic and optical properties of these compounds. For example, it is responsible for the one-dimensional conductivity in segregated stack compounds such as TTF-TCNQ; but this high conductivity is relatively rare. In the mixed-stack D-A (1:1) CT-compounds, such as TTF-CA, TTF-BA, TMB-TCNQ, TMPD-CA, DMTTF-CA, etc. (see [1] for a zoological description), the charge transfer occurs within the chains and all these compounds are small-gap semiconductors.

Some of those mixed-stack compounds exhibit uncommon electronic instabilities, which give rise to different types of reversible structural transitions under pressure, temperature or photo-irradiation. A common feature of all these transitions is the loss of symmetry-inversion in the crystal below a critical temperature T_c or above a critical pressure P_c .

This symmetry breaking is accompanied by a more or less abrupt variation of the charge transfer. In the vicinity of the transition, very interesting and puzzling phenomena are observed: colour variation, precursor effects, phase-coexistence and thermal hysteresis, disorder, etc., and also non linear excitations.

The aim of this highlight is to review the essential aspects of the observed instabilities. For the sake of "simplicity", it will be focused on the 1:1 mixed-stack compounds, disregarding more complex structures such as the D_2A packings, which generally do not form well defined stacking chains.

2 Structural properties

What is striking when considering the structural data at room temperature is the great diversity of possible crystalline structures for compounds constituted with very similar molecules.

Some of them exist in different structures at room temperature and atmospheric pressure: for example monoclinic and triclinic TMB-TCNQ [2, 3], or green (mixed-stack) and black (segregated) phases for TTF-CA [4].

Also, it seems hopeless to try and find any systematics in the structural properties of whole families such as the tetrathiafulvalene-tetrahalo-p-benzoquinones, or TTF-A (A = FA: Fluoranil, CA: Chloranil, BA: Bromanil, IA: Iodanil), of general formula $C_6S_4H_4-C_6X_4O_2$. These four compounds form indeed mixed-stacks, but in different structures: TTF-FA and TTF-IA are triclinic with one TTF and one FA or IA entity per unit cell, pertaining to one chain [5, 6]. Green TTF-CA is monoclinic $P2_1/n$ with two TTF and two CA per cell (two equivalent chains) [5], whereas TTF-BA forms two non-equivalent and non-parallel chains in a triclinic structure [7]. The situation is far more complex than in "standard" metallic and semi-conducting compounds, and in those conditions, no obvious trends can be deduced from simple considerations such as the increasing electronegativity in the halogen series: at room temperature TTF-FA, TTF-CA and TTF-IA are nearly neutral, whereas TTF-BA is ionic.

3 What is known concerning the two phases

The structural and dynamical effects associated with the phase transitions in the 1:1 CT complexes have been studied for many years, mainly in US, Japan, Italy and France. For some of these materials, especially TTF-CA, an ensemble of fundamental physical properties has been analysed, which can be used as a guide and control for theoretical investigations:

- The variations of the intra- and inter-molecular vibration modes have been measured by infra-red and Raman spectroscopies [4, 8]. The appearance of new IR lines of a_g symmetry below T_c or above P_c is the clear signature of the loss of the center of inversion. These experiments are therefore among the most important tools for analysing the transitions.

- The exact positions of the atoms in the high symmetry phase have often been obtained by X-ray measurements [5, 7]. For TTF-CA, an analysis of the structural changes at the transition (which symmetry-elements are lost?) has been performed by neutron diffraction [9] and NQR [10]. A distortion of the molecules has been observed in the low symmetry phase, accompanied by a weak "dimerization" along the stack (weak D-A pairing by a reduction of $\simeq 0.1\text{\AA}$ (2%) of their intermolecular distance). In other compounds, the loss of centrosymmetry has also been interpreted as a dimerization (as the most probable way by which it can happen), though the corresponding molecular displacements have not been estimated.

- The width of the electronic gap is estimated from the position of the "charge transfer excitation band" in the polarized reflection spectra [11, 12]. It is of about 0.8 to 1 eV in TTF-CA.

- The value of the charge transfer in each crystalline phase is deduced in an indirect way (which will be discussed hereafter) from Raman, infra-red and reflectivity measurements [12, 2].

- The magnetic state of the compounds is obtained from susceptibilities deduced from ESR experiments [8, 13].

- An estimate of the entropic contribution to the free energy at the transition has been deduced from specific heat measurements [14].

4 Which kind of transition?

The common characteristic of the structural transitions observed in these compounds is the appearance of an electric polarization along the chains below T_c or above P_c . However, there is an important qualitative difference with respect to the standard ferroelectric transitions occurring in ionic compounds such as $BaTiO_3$:

Instead of single ions, the sites here are large deformable molecules and the molecular

orbitals involved in the charge transfer and the polarization are constructed by linear combinations of a dozen of atomic wave-functions. This allows more complex electronic configurations and several original phenomena accompanying these transitions have been observed.

The two phases have been *a priori* characterized by two parameters: the **charge transfer** ρ between D and A , and the **dimerization parameter** η , which represents the displacements of the molecules in the low symmetry phase, with respect to equidistant positions along the chains. There exists experimental evidence that the coupling between these two parameters is complex, since very different behaviours are observed at the transition for compounds presenting only small structural or chemical differences:

-TTF-CA [12] is the prototype for the "neutral to ionic" transition. The "neutral" phase, at high temperature or low pressure, is non-dimerized, with a weak charge transfer ($\rho \simeq 0.3e^-$) from TTF to CA. This charge transfer undergoes a sudden jump at $T_c \simeq 80K$, and reaches a value of about $0.7e^-$ in the low temperature dimerized phase ("ionic" phase).

- In TTF-BA [7], in which the four chlorine atoms of CA are replaced by four bromine atoms, a "dimerization" (i.e. a loss of centrosymmetry) occurs at the transition temperature ($50K$), without any noticeable change in the degree of ionicity ($\rho \simeq 0.8e^-$ in both phases).

It must be noted here that this charge transfer and its variation have to be shared among all the atoms of each molecule, so that the corresponding value for each atom is very small ($\simeq 0.1e^-$ or less), and could be accounted for by small deformations of the molecular orbitals.

Magnetism plays also a great part in the nature of the transition. Most of the compounds considered here are diamagnetic in the dimerized phase, apart from a weak paramagnetic susceptibility attributed to intrinsic defects (see below). The standard explanation for this is the formation of $S=0$ electronic states due to the pairing of the D^+ and A^- molecules. Their magnetic behaviour at high temperature together with the charge transfer variation and the structural data have been used in the literature to classified the mixed-stack compounds in several categories, according to the principal characteristics of their transitions:

1 - Some compounds remain diamagnetic in the non-dimerized phase. This is quite understandable in the case of TTF-CA, where the molecules become suddenly nearly neutral above T_c . This is a typical **neutral to ionic** transition. Due to its similar magnetic behaviour, monoclinic TMB-TCNQ has also been classified in that category [3] though in this compound the charge transfer discontinuity is much smaller ($\Delta\rho \simeq 0.1e^-$) [2]. By extension, its high temperature phase is also called "neutral" phase, despite its non-negligible ionicity ($\rho \simeq 0.6e^-$).

2 - In TTF-BA, the charge transfer is relatively high in both phases, without discontinuity at the transition. The high temperature phase is paramagnetic (and not neutral!), with probably an antiferro- or ferri-magnetic coupling between adjacent D and A molecules. The similarity of its susceptibility with what is obtained in an Heisenberg linear chain of spins $1/2$ [7] suggests here a **spin-Peierls** mechanism for the transition.

3 - For triclinic TMB-TCNQ, where ρ keeps an intermediate value of about $0.6e^-$, the magnetic susceptibility remains weak in both phases [3]. The only noticeable anomaly is in the dielectric constant, so that the transition is only characterized by the **ferroelectric** ordering along the chains, induced by the dimerization.

4 - TMPD-CA has to be considered separately [8]. The estimated degree of ionicity is also of about $0.6e^-$ in both phases. But the vibrational spectra show that the stack is dimerized even at room temperature, and that the high temperature phase is characterized by a non-negligible disorder due to tilting and distortion of the molecules. In that case, the transition is supposed to be of an **order-disorder** (orientational) type.

The transition itself is often a first order one, but its characteristics vary in the different compounds and for different experimental conditions: for example, the charge transfer discontinuity is weaker and the thermal hysteresis larger in monoclinic TMB-TCNQ than in TTF-CA. Under increasing pressure, this discontinuity decreases [15, 16] suggesting possible existence of a critical point beyond which it would be of second order. On the other hand, a large domain of coexistence of the two phases can be observed in some compounds (e.g. DMTTF-CA [17]).

5 Charge transfer and vibration modes

A fundamental parameter characterizing the high and low symmetry phases is the charge transfer ρ from D to A . Therefore, its precise experimental determination is of foremost importance. The value of ρ is principally extracted from the IR and Raman spectra, by assuming a linear variation of the frequency of specific intramolecular modes with ionicity, which are assumed to be otherwise unperturbed by environmental effects. Extensive work [18] on TTF-X-p-benzoquinones has shown that two categories of intra-molecular modes are particularly interesting:

- The a_g totally symmetric modes (with respect to the isolated molecule point group), which are Raman active and are observable in the IR spectra only in the absence of

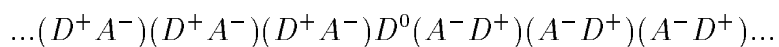
the center of inversion. They are coupled by symmetry with the electrons, so that their frequency variation versus ρ may be highly nonlinear. In the literature, this coupling with the electrons is often called e-mv (i.e. electron-molecular-vibration) coupling, or vibronic interaction.

- The b_u non-symmetric modes, which are only observable in the IR spectra and whose frequencies can be used as ρ probes by interpolating between the corresponding frequencies of the fully neutral and fully ionic species. The step-like curve of ρ versus temperature presented in the literature for compounds undergoing a neutral to ionic transition [2, 12] is in fact a direct translation of the step-like variations of their intramolecular modes versus temperature.

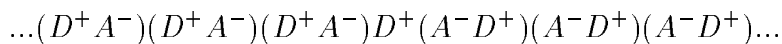
However, experimental tests on the linear variation of these b_u modes in TTF derivatives have revealed some anomalies, and no such check can be made for the CA molecule, in the absence of synthesized compounds where a partial degree of ionicity could be supposed to be fixed by stoichiometry [4]. The charge transfer in those compounds is nevertheless extracted from the "most reliable" intramolecular vibrations, for example the b_{1u} C=O stretching mode of CA in TTF-CA. It is obvious that due to the importance of this parameter in the analysis and modelization of the transition, the assumption of linearity has to be somehow verified, at least by theoretical simulations when no direct experimental control seems possible.

6 Domain walls and dynamical properties

One of the most interesting originalities in the series of mixed-stack compounds is that a wide range of dynamical properties: non-linear conductivity, magnetic susceptibility, ESR motional narrowing [19], dielectric response [21], spin-lattice relaxation time [20], etc., is connected to the existence of localized defects, which are mobile along the chains near the transition. In the low temperature phase, their concentration (estimated from susceptibility measurements) is about 10^{-5} per unit cell. They are identified with intrinsic phase mismatch defects in the lattice, such as soliton-like defects in polyacetylene [22] or in halogen-bridged Pt or Pd complexes (often called MX chains) [23]. They correspond to domain walls between ionic states of opposite polarizations in the ionic phase, carrying a charge or a spin:



or



In the neutral phase, they correspond to fluctuating ionic domains just above T_c :

$$\dots D^0 A^0 D^0 A^0 (D^+ A^-) (D^+ A^-) (D^+ A^-) D^0 A^0 D^0 A^0 \dots$$

The detailed study of the dynamics associated to these domains is of course a key for the understanding of these systems.

7 Models

It seems obvious that these transitions result from a delicate interplay between electronic, magnetic and dynamical interactions in the crystal. The first empirical attempts to explain these phenomena relied on a competition between the energy cost of the transfer of one electron from D to A (which can be estimated from the difference between the ionisation energy of D and the affinity of A) and the Madelung energy gained in this transfer [11, 24]. However, several other parameters have to be taken into account to obtain a quantitative description of these transitions: electronic charge transfer integrals, on-site Coulomb repulsion, coupling with the phonons, etc.

Later on, theoretical studies of these phase transitions have been developed, principally based on expansions of the free energy of the crystal [25, 26], or on one dimensional model-Hamiltonians of Su-Schrieffer-Heeger or extended-Hubbard type [27]. These Hamiltonians are similar to those which were devised to study the elementary excitations (solitons, polarons) in polymeric chains such as polyacetylene [22].

In these models, each molecule is represented by one orbital on a fictitious particle in a one-dimensional chain. The most complete Hamiltonian that has been considered can be written as:

$$\begin{aligned} H = & \sum_{l,\sigma} T_{l,l+1} (C_{l,\sigma}^+ C_{l+1,\sigma} + C_{l+1,\sigma}^+ C_{l,\sigma}) + \frac{\Delta}{2} \sum_l (-1)^l n_l \\ & + U \sum_l n_{l,\uparrow} n_{l,\downarrow} + V \sum_l n_l n_{l+1} + K \sum_l (u_l - u_{l+1})^2 \end{aligned}$$

The orbitals with even and odd l represent respectively the LUMO (lowest unoccupied molecular orbital) of A and the HOMO (highest occupied molecular orbital) of D . $C_{l,\sigma}$ ($C_{l,\sigma}^+$) is the annihilation (creation) operator of an electron at site l with spin σ , and $n_{l,\sigma}$ the corresponding number of electrons. Here $T_{l,l+1}$ is the electron transfer, Δ is the site energy difference between D and A molecules, U is the on-site Coulomb repulsion, and V is the Coulomb interaction between nearest neighbours. Finally, K represents the

electron-lattice interaction, u_l is the particle displacement along the stacking axis. $T_{l,l+1}$ is supposed to vary linearly with $u_l - u_{l+1}$.

Obviously, simulations lead to various kinds of transitions (with or without charge transfer variation, with or without dimerization) depending upon the choice of the values of the parameters T , Δ , U , V and K . In the most explicit calculations, the transition has been studied as a function of Δ for fixed values of T , U and V . The introduction of the electron-phonon coupling K was necessary to reproduce the right values for ρ in both phases of TTF-CA, but it smoothed out its variation at the transition.

These schematic models give a general description of the sensitivity of a class of materials to the magnitude of the different interactions. However, they have no direct relation to the experimental results for one precise compound, due to the impossibility of fixing a set of parameters which would be really specific to this compound. Moreover, they cannot analyse the interplay between electronic distribution and dynamics at the atomic level.

8 Are they as low-dimensional as that?

The anisotropic character of these crystals has been observed in their polarized light optical properties, parallel or perpendicular to the chains. On the other hand, the strong anisotropies obtained in the dynamical properties near the transition (dielectric constant, conductivity) are due to intrinsic defects mobile along the chains. There are however some indications that the three-dimensional aspects may be important in the interpretation of the experimental data.

In most of these compounds, the particularly flat character of the molecules is enhanced by the fact that they are tilted with respect to their stacking axis and often form in two other directions, very well defined planes containing molecules of both species, pertaining to different stacking chains. For someone who is not concerned with the "linear chain" aspect, the resulting structure can be described in a more precise way by a stack of interacting parallel molecular planes. Those planes are conspicuous in structures already published such as TMB-TCNQ [2], or TTF-p-QC1₂ [30], which is a fifth member of the family of TTF-X-p-benzoquinones, obtained by replacing two equivalent Cl atoms of CA by two hydrogen atoms (triclinic, 1 chain/cell). They are also visible in green TTF-CA [9] but form in that case two intersecting stacks of planes due to the existence of a gliding mirror connecting the two equivalent chains in the unit cell.

The fact that the molecules are arranged in such a peculiar way shows that the "inter-chain" interactions, which are in great part "intra-plane" interactions, are of foremost importance in the stability of the structure. In particular, the interactions between the hydrogen atoms of TTF and the halogen and oxygen ones of the neighbouring X-p-benzoquinone should be

considered with special care. Moreover, it would also be interesting to understand the very different crystalline structure of TTF-BA, with two crossed linear chains and no obvious molecular planes, which is certainly connected to its different behaviour.

The intra-chain interaction is probably the strongest interaction in the crystal. From a pure geometrical point of view, it couples the successive above-mentioned molecular planes. Its analysis helps to clarify the analogies which have been made between those CT complexes and polyacetylene or MX chains.

It has been known for a long time (and it is easy to show by ab-initio calculations [28]) that the molecular orbitals involved in the crystalline structure: the LUMO of the acceptor A and the HOMO of TTF in TTF-p-benzoquinones, are formed from linear combinations of p-atomic orbitals pointing perpendicularly to the molecular planes and coupled by π interactions. Due to the tilt of the molecules with respect to the chain, the interaction between the molecular orbitals occurs in a zig-zag way rather than exactly along the stacking axis: a given A molecule interacts more strongly with the right part of the TTF molecule situated just below, and the left part of the one just above [5, 8].

Nevertheless, this inter-molecular interaction is much more of σ than of π type, which makes an essential difference with polyacetylene, apart from the fact that the two partners of the pair here are of different chemical species. It resembles more the type of interactions occurring between the d_{z^2} orbitals of the metal and the p_z orbitals of the halogen atom in the MX chains. Therefore, the recent ab-initio theoretical studies performed by Alouani et al. [29] on the dimerization in these mixed-valence halogen-bridged CT complexes are particularly interesting. These calculations were able to explain the origin of the charge density waves (CDW) observed in the Pt and Pd based compounds, as well as the spin density waves (SDW) in Ni based compounds. Especially, they have shown that the inter-chain interactions, propagated through ligands surrounding the metal atoms, are necessary to generate the insulating ground state and the lattice distortion observed in the Pt based compounds.

However, the analogy with the organic complexes should be considered with some caution: instead of a "dimerization": $\dots XM - XM - XM\dots$, the transition in the Pt and Pd based MX chains induces a doubling of the unit cell by creating an alternation of isolated M atoms and triplets XMX along the chains: $\dots M - XMX - M - XMX\dots$, with non-negligible atomic displacements ($\simeq 10\%$).

A point which is worth noticing in these comparisons concerns the non-linear excitations. The large enhancement of σ or ϵ in the vicinity of T_c [19, 21] is attributed to the increased mobility of intrinsic defects of soliton-type, associated with the domain walls. This type of excitations exists also in polyacetylene and some MX chains, inducing the appearance of an absorption peak in the middle of the gap. It is very interesting to remark that

this extra-peak does not appear in MX-materials with strong inter-chain interactions [23]. Such an analysis of the absorption spectra below the charge-transfer peak in the 1:1 CT complexes (which is lacking) would give valuable information on the strength of the inter-chain coupling in these compounds.

Finally, it must be noted that, when going beyond the usual picture of solitons moving along linear chains, it is difficult to visualize in 3-dimensions those domain-walls and their displacements. Due to the very weak dimerization observed in some of these CT complexes, they may correspond to weak displacements of the above mentioned molecular planes, accompanied by distortions of the molecules in these planes. Pending new crystallographic studies in the low temperature or high pressure phases for most of these compounds, this is still an open question.

It will most probably be necessary to take properly into account those 3-dimensional interactions to reproduce correctly the subtle transitions occurring in the 1:1 CT organic compounds. This is confirmed experimentally by the fact that, in TTF-CA, the unit cell undergoes a small discontinuous contraction just at the transition temperature, in the directions \vec{b} ($\simeq 0.5\%$) and \vec{c} ($\simeq 0.1\%$) i.e. roughly perpendicularly to the direction \vec{a} of the chains [9]. This implies a discontinuity in the inter-chain interactions at the transition.

The lattice contraction, coupled with the charge-transfer discontinuity, induces also a sudden variation of the Madelung energy of the crystal. This Madelung energy is an important factor of stabilization of the ionic phase. Nevertheless, it is usually reduced in the model Hamiltonians to the nearest neighbour Coulomb interaction *along* the chains, which completely neglects the implications of its 3-dimensional character.

9 Perspectives

It is now possible to tackle these problems by ab-initio self-consistent numerical techniques. These calculations should give a really local description of the crystal on both sides of the transition: variation of the ionicity of each atom, charge transfer between the molecules and Madelung energy in the crystal, total energy, forces and relaxations, etc., i.e. quantities which are related to the experimental results obtained for these materials. The direct calculation of the charge transfer can be compared to its indirect experimental determination deduced from vibration spectra; the self-consistent determination of the potential on each atom may help to interpret local measurements such as the NQR on the Cl atoms in CA [10]; these calculations could also be useful for a less ambiguous determination of the parameters entering the Hubbard-like Hamiltonian describing the actual transitions.

The aim of these studies is to build a general theoretical scheme in the frame of which all

the different mixed-stack compounds and their different behaviours could be described, on the same footing, in a quantitative way.

Several numerical codes based on similar techniques are now available. These techniques rely on different basis-sets for the description of the electronic structure within the Local Density Approximation (LDA) or on more sophisticated treatments of electronic exchange and correlations: Linear Muffin-Tin Orbitals (LMTO), plane waves (LAPW), Projected Augmented Waves (PAW) [31], etc. The latter is coupled to molecular dynamics calculations, so that it allows straightforward relaxations, finite temperature simulations and ab-initio determinations of the eigenfrequencies and eigenvectors of the molecular vibrations [32].

Our preliminary results in this domain seem promising. The nature of the intra-chain interactions can be analysed [28] with the help of a full-potential LMTO code which has been devised to study the dimerization along linear polymeric chains [33]. The importance of the inter-chain interactions can be studied with the use of a faster LMTO-ASA 3-dimensional code [34]. For example, we have obtained with this code a small gap and a reasonable value of the charge transfer in TTF-p-QC l_2 [35]. With the PAW program, it has been possible to prove numerically that for an isolated charged CA molecule, the C=O stretching mode indeed varies linearly with the charge [36]. This provides the necessary confirmation of the empirical rule from which the experimental value of the charge transfer is extracted.

The difficult points in those calculations are the large number of atoms and the molecular character of the crystal, i.e. the importance of the interstitial region. In these weakly interacting systems, the exchange and correlation interactions have to be treated carefully, which requires to go beyond the possibilities of the LDA (self-interaction, non-local corrections, etc.).

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- DMTTF = 2,6-dimethyltetrathiafulvalene ($C_8 S_4 H_8$)
- TMPD = tetramethyl-p-phenylene ($C_{10} N_2 H_6$)
- TMB = 3,3',5,5'-tetramethylbenzidine ($C_{12} N_2 H_{16}$)
- TCNQ = tetracyanoquinodimethane ($C_{12} N_4$)
- CA = tetrachloro-p-benzoquinone or chloranil ($C_6 Cl_4 O_2$)
- BA = bromanil ($C_6 Br_4 O_2$)
- etc...

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