Ψ_k Newsletter

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

Number 53 October 2002

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Contents

1 Editorial

There are several interesting items in this newsletter and among them the scientific highlight of the month by Mariusz Krawiec (Bristol), one of the RTN1 (RT Network on Computational Magnetoelectronics) postdocs, on **"Ferromagnet/Superconductor Heterostructure"**. We also have a number of short scientific highlights by this network in their **News from the RTN1** section. In the **News from the ESF Programme** section there are two workshop/conference reports that also include abstracts of presented papers. More abstracts can be found in the dedicated **Abstracts** section. In the **News from the ESF Programme** section readers can also find a report by Volker Heine on a visit to European Commission to discuss creation of infrastructures within the 6th framework. The **General News** section contains some information on the Psi-k web pages. As usual, we have a number of position and workshop/conference announcements in this newsletter. In particular, we would like to turn readers attention to the conference in Bristol, UK, to take place in April next year. This conference is dedicated to Prof. Balazs Györffy (Bristol University) to celebrate his many important contributions to the theories of the solid state physics on the occasion of his 65th birthday. Balazs is one of the prominent members of our Psi-k community and we would like to make this conference a success. Do try to participate. The conference scope is quite broad and its title is **"Order and disorder in solids: alloys, magnetism and superconductivity"**. Please check the table of contents for further details.

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

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

The above contains information on the Psi-k 2002 workshops and hands-on courses. In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

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

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

2 General News

2.1 Psi-k Web Pages

The Psi-k web page was updated over the summer and it should be better accessible with the Netscape browser. This web contains information on the Psi-k workshops and hands-on courses as well as being the repository of the Psi-k newsletters and highlights. We have now also started to collect the URL's of available electronic structure codes, both the public domain and the commercial ones. If you wish your URL to be incorporated in this list please e-mail this to psik-coord@dl.ac.uk. Any suggestions on how to make the Psi-k web pages more useful will be gratefully received.

3 News from the Research Training Network 1 (RTN1)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 Scientific Highlights of the RTN1

The second annual meeting of the RTN Computanional Magnetoelectronics will take place in Oléron Island (France) from October 5 to October 9. The programme of the meeting can be found on the web site:

http://psi-k.dl.ac.uk/magnetoelectronics/report_2002.html.

Part of this annual meeting is also the mid-term review of this Network which started on October 1 2000. Below the reader can find the highlights of this Network so far.

Electronic structure and tunnel magnetoresistance of Fe/MgO/Fe

M. Bouhassoune, A. Ernst, J. Henk, and P. Bruno, *MPI für Mikrostrukturphysik Halle, Germany*

M. Däne, D. Ködderitzsch, W. Hergert, and I. Mertig, *University Halle-Wittenberg, Germany*

Z. Szotek and W.M. Temmerman, *Daresbury Laboratory, UK*

Understanding of tunneling magnetoresistance (TMR) is necessary for the important development and fabrication of magnetic tunnel junctions (MTJ) used in non-volatile memories (MagneticRAM). A prototypical system for such a tunnel junction is Fe/MgO/Fe. It has the advantage that the insulating material is ordered and therefore well characterised. Recent work from the experimental group at the MPI in Halle (PRL **87**, 076102 (2001)) established that an FeO interface layer is grown between Fe and MgO and that a substantial interface relaxation takes place. We have started a systematic study on how the electronic structure is affected by (1) interfacial structural relaxation, (2) oxidation of the Fe interface layer, (3) correlation effects in the FeO interface layer, (4) non-stoichiometry in the FeO interface layer. In conjunction with this we also investigate how these effects influence the tunnelling conductance. Our specific findings so far are: (1) structural relaxation at the interface induces an anti-parallel Fe spin magnetic moment in the layer adjacent to the Fe interface layer, (2) a substantially enhanced Fe spin moment in the interface layer is due to oxidation induced correlation effects, and (3) the spectral functions at the Fermi level with and without oxidation of the Fe interface layer differ quite dramatically. The resulting changes in the conductances are shown on the front cover of the mid-term review report.

Dilute Magnetic Semiconductors

I. Abrikosov, O. Eriksson, and S. Mirbt, *University of Uppsala, Sweden*

J. Kudrnovský, I. Turek, V. Drchal, and F. Maca, *Academy of Sciences, Czech Republic*

K. Sato and P.H. Dederichs, *Research Center Juelich, Germany*

P. Mohn and P. Weinberger, *TU Vienna, Austria*

The recent discovery of $Ga_{1-x}Mn_xAs$ as a ferromagnet with a Curie temperature of 110K has initiated strong research activities on dilute magnetic semiconductors (DMS) since these materials might enable an all-semiconductor spinelectronics. In the last year three groups of our Network have given important contributions to this young field which are fundamental for the understanding of these compounds and for the search for new DMS with high Curie temperatures.

The Swedish/Austrian group has resolved the conspicuous disagreement between previously calculated ($4\mu_B$) and measured $\sim 2\mu_B$) magnetic moments per Mn atom in (Ga,Mn)As. By considering a partial compensation of the holes in the Mn gap states by As antisites, they show that the ferromagnetic state is destabilised in favor of a ferrimagnetic state with non-collinear moments, yielding a strongly reduced macroscopic moment, as measured in experiment, while at the same time the absolute value of the moment per Mn atom approaches $5\mu_B$. The Swedish group could give an explanation of the gap states in terms of As dangling bonds. The Czech/Austrian group has extended this work on (Ga,Mn)As by a detailed study of the non-collinear behaviour and an estimation of the Curie temperature within the mean field approximation of the Heisenberg model. Assuming a reasonable concentration of As antisites, the calculated Curie temperature is in qualitative agreement with the experiment. The Juelich group has considered a broad range of different DMS systems. Based again on the mean field approximation their results predict that very large Curie temperatures can be obtained, lying above room temperature in the cases of (Ga,Mn)N, (Ga,Cr)N, and (Ga,Cr)As. For small concentrations x of the transition metal atoms, the Curie temperature increases as x, which can be explained by the double exchange mechanism.

Magnetic and transport properties of ferromagnet/semiconductor/ferromagnet systems

V. Popescu and H. Ebert, *University Munich, Germany*

N. Papanikolaou, P. H. Dederichs, and R. Zeller, *Research Center Juelich, Germany*

A very flexible computer program has been developed that allows to study the magnetic and transport properties of arbitrary bulk and layered systems in an ab-initio manner. The underlying electronic structure is calculated in a fully relativistic way by means of the tight-binding version of the Korringa-Kohn-Rostoker method on the basis of the Dirac-equation. This rather general approach allows in particular to study spin-orbit induced properties as for example the magneto-crystalline anisotropy, orbital magnetic moments and the magnetic circular dichroism in X-ray absorption. Alloy systems and interdiffusion at interfaces are accounted for by making use of the Coherent Potential Approximation. Transport properties of layered systems are treated with making use of the Landauer-Büttiker-formalism as worked out by Stone and Barranger.

Recent applications of the program package concentrated on the influence of spin-orbit-coupling

on the magnetic and transport properties of ferromagnet/semiconductor/ferromagnet trilayer systems. Similar to the situation for a noble metal spacer material a strong enhancement of the spin-orbit induced orbital magnetic moment at the ferromagnet/semiconductor-interface was found as for example for Fe in Fe/GaAs/Fe. Concerning the transport properties of Fe/GaAs/Fe-trilayer systems similar results have been obtained as previous non-relativistic calculations. Inclusion of spin-orbit coupling reduces the conductance in general by several percents depending on the thickness of the semiconducting spacer. Since this reduction is more pronounced for the anti-ferromagnetic spin-configuration an appreciable reduction of the TMR ratio results. The great flexibility of the program package opens the way to study many interesting problems in magneto-electronics.

A self-consistent treatment of non-equilibrium spin torques in magnetic multilayers

Asya Shpiro and Peter M. Levy, *New York University*

Shufeng Zhang, *University of Missouri-Columbia*

Albert Fert, *Unité Mixte de Physique CNRS/THALES, and University Paris-Sud, Orsay*

Ballistic transmission across an interface is not the only physics of transport in magnetic multilayers. Therefore interface ballistic spin transfer, which has been the center of the previous discussions should be embedded in a larger picture, i.e., the ballistic transport across an interface should be connected to the diffusive transport outside the interfacial region. We have calculated the spin torque for a model system consisting of a magnetic multilayer whose essential elements consist of a thick magnetic layer, whose primary role is to polarize the current, a thin magnetic layer that is to be switched, a nonmagnetic spacer layer so that there is no interlayer exchange coupling between the thick and thin layers, and a nonmagnetic layer or lead on back of the thin magnetic layer. We have found the unanticipated result that the angular momentum transferred to a thin layer far exceeds the transverse component (to the orientation of the magnetization of the thin layer) of the bare portion of the incoming spin polarized current, i.e., that part proportional to the electric field. It is a direct consequence of the spin accumulation coming from the two primary layers, the thick magnetic and nonmagnetic back layers, that produce this buildup. The exchange interaction between the conduction electrons and the magnetic background produces the transfer of spin angular momentum between the current , via the accumulation, and the magnetic background; this is not a diffusive process. Among other things the parameters entering our theory are determined from CPP transport measurements, except for the exchange interaction between the itinerant electrons and the magnetic background.

Electronic and magnetic properties of half-metallic oxides

Z. Szotek, G. Banach, and W.M. Temmerman, *Daresbury Laboratory, UK*

A. Barthélémy, M. Besse, M. Bibès, M. Bowen, V. Cros, H. Jaffrès, F. Petroff and A. Fert , *CNRS/ Thales, France*

D. Ködderitzsch, W. Hergert, and I. Mertig, *University Halle-Wittenberg, Germany*

In the field of spin electronics, the search for new half metallic materials with a high Curie

temperature represents a very important challenge. Such materials whose conductivity is fully spin-polarized are highly desirable for utilization as electrodes for spin valves, magnetic tunnel junctions and logic devices. The fundamental electronic and magnetic properties of several oxide materials were investigated: (1) the spin magnetic moments and their orientation in the family of the double perovskites and in particular Sr_2FeMoO_6, (2) magnetite Fe_3O_4, (3) $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and (4) vacancy induced half-metallicity in NiO. So far we have: (1) established that the half-metallicity in Sr_2FeMoO_6 is due to a configuration with five localized d electrons forming a high spin moment on Fe and one antiparallel delocalized electron shared between the Mo and the other sites, (2) demonstrated that the ionic charge ordered state in Fe_3O_4 is not the state with the lowest energy, it is rather the Fe^{3+} state on all the tethrahedral and octahedral sites, (3) showed that half metallicity occurs in LSMO for Mn^{3+} only and a record tunnel magnetoresistance of more than 1800 % was measured in LSMO/$SrTiO_3$/LSMO epitaxial tunnel junctions. Finally (4) a new family of half metallic oxides was explored and half metallicity was found in vacancy "doped" NiO.

The role of interfaces in the magnetoresistance of realistic spin valve systems

P. Weinberger, J. Zabloudil, R. H. Hammerling, *Technical University of Vienna, Austria*

L. Szunyogh, *Budapest University of Technology, Hungary*

By using the fully relativistic spin-polarized screened Korringa-Kohn-Rostoker method and the corresponding Kubo-Greenwood equation, resistivities and the current-in-plane giant magnetoresistance (CIP-GMR) are evaluated for Fe/Au/Fe/Au spin valves assuming both bcc-like Fe and fcc-Au leads and compared to experimentally obtained data by B. Heinrich et al. At T = 10 K the experimental values are 5.6522 and 5.8175$\mu\Omega$cm in the parallel and the antiparallel case, respectively. This corresponds to a GMR of 2.84%, using the so-called pessimistic definition. At room temperature the values for the resistivities are roughly twice as large and lead to a GMR ratio of 1.72%. All experimental measurements were performed placing the contacts on the Au parts of the system.

The theoretical resistivities corresponding to systems with an Fe-substrate are almost a factor of 2 bigger than those referring to systems with a Au-substrate. For large interdiffusion concentrations, the GMR for the two types of systems (Au and Fe substrate) are about the same, crucial differences occur in the regime of very small interdiffusion: for vanishing interdiffusion the GMR for the spin-valve with the Au-substrate becomes rather small. In this particular case (no interdiffusion, Au substrate) the theoretical values are 1.4003 and 1.4355$\mu\Omega$cm in the parallel and the antiparallel case, respectively; the corresponding GMR amounts therefore to 2.45%. Since this particular set-up (Au-substrate) mimicks most closely the experimental situation, these theoretical results compare extremely well with the experimental data: the GMR value is almost the same, the resistivities are only about a factor of 4 too small.

Current Carrying Ground States in Ferromagnetic-Superconductor Nanostructures

M. Krawiec, B.L. Gyorffy and J.F. Annett, *University of Bristol, UK*

The Proximity effect between a superconductor and a non-superconducting metal is dramatically

different if the latter is a ferromagnet. This has been realized only recently and the subject is of considerable current interest. In particular, much attention is focused on the surprisingly long range and oscillatory behaviour of the pairing amplitude in the ferromagnet. Prompted by the similarity of this phenomenon to that prevailing in π-junctions we have studied the possibility that such heterostrucures carry current even in their ground state. To address all the issues at stake on equal footing we have solved a simple lattice-model representing an insulator-metallic ferromagnet-superconductor trilayer exactly, albeit numerically. In short, we have determined the pairing potential χ,magnetization m and the current j selfconsistently. We discovered that the ground states generically carries a current which flows in the opposite direction on the two sides of the superconductor-ferromagnet interface and parallel to it. Moreover, we found that this current is spin-polarized under most circumstances. We have submitted three paper on this subject for publications are now working on identifying experimental manifestations of this novel phenomenon and devising ways of exploiting it in 'spintronics' applications.

Spin torques in ferromagnetic/normal metal structures

G.E.W. Bauer, *TU Delft. The Netherlands*

K. Xia, P.J. Kelly, *University of Twente, The Netherlands*

I. Turek, *Academy of Sciences, Czech Republic*

The experimental observation of current induced magnetization reversal ("spin transfer") calls for a general framework for describing electrical transport in non collinear and disordered magnetic systems. A circuit theory was formulated based on kinetic equations for spin currents (A. Brataas et al., PRL 84, 2481 (2000)) which is nearly equivalent to a random matrix theory of transport generalized to magnetic heterostructures but considerably more flexible. A central parameter in the circuit theory is a so called spin mixing conductance G^{mix}, in addition to the usual spin up and down conductances $G^{\uparrow}$ and $G^{\downarrow}$. It turns out that G^{mix} is the only material dependent parameter entering the expression for the magnetization torque. G^{mix} also determines the angular magnetoresistance (aMR) of perpendicular spin valves and therefore can be extracted from aMR measurements, or via the excess Gilbert damping of the magnetization dynamics in multilayers (Y. Tserkovnyak et al., cond mat/0208091).

The ubiquitous appearance of G^{mix} in various physical properties motivated us to calculate it from first principles together with $G^{\uparrow}$ and $G^{\downarrow}$ for a number of materials systems of current interest using a recently developed parameter free scheme for calculating the transmission and reflection matrices required in the Landauer Büttiker formulation of transport theory (K. Xia et al., PRB 63, 064407 (2002)). The values of G^{mix} calculated for Fe/Cr and Co/Cu interfaces do not depend critically on the materials making up the interfaces and are in quite good agreement with values extracted from aMR measurements by the Michigan State University group an Py/Cu.

Knowledge of G^{mix} allows the torque to be calculated if the spin accumulation is known. Because the mixing conductance mainly contributes to the torque while $G^{\uparrow}+G^{\downarrow}$ known determines the electron current, it is interesting to compare $|G^{mix}|$ with $G^{\uparrow}+G^{\downarrow}$. Large values of $|G^{mix}|$ $/(G^{\uparrow}+G^{\downarrow})$ mean more torque per unit current. An unexpected result of the calculations (K. Xia et al., PRB **6**5, 220401 (2002)) was that the spin mixing conductance in tunnel junctions can

remain large even when the conventional conductance itself is made vanishingly small. This can be achieved in a three terminal "spin flip transistor" device (A. Brataas et al., PRL **8**4, 2481 (2000)) in which a spin-current is injected in the absence of an electron current. In practical memory devices it may be advantageous to be able to achieve such a separation of particle and spin injection. Furthermore, the torque turns out to be larger and less dependent on the angle in a three- than a two-terminal device.

4 News from the ESF Programme

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

4.1 Report on a visit to European Commission

Brussels, 22 August, 2002

A group of four of us visited the European Commission (EC) on 22 August, 2002 for a detailed discussion with Dr Daniel Pasini, who is in charge of the scheme on Integrated Infrastructure Initiatives (abbreviated as I3) in the new EU Framework Programme FP6. Our team consisted of myself as chairman of Psi-k, Prof. Walter Temmerman as secretary of Psi-k, Prof. Michel Mareschal as director of CECAM, and Prof. Paul Durham as head of theoretical physics and computational science at CCLRC Daresbury Lab..

The purpose was to discuss whether the research community covered by the two ESF Programmes Psi-k and Simu could propose an I3 for computer simulation of materials based on CECAM, Daresbury and seven other centres across Europe.

Dr Pasini himself is a plasma physicist, and the EC has in the past focused on large hardware installations, libraries and databases as infrastructures, though centres of expertise can now be included. From our point of view the networking etc. activities of Psi-k and Simu clearly provide the kind of know-how and software infrastructure needed by researchers in our community, but equally clearly this is stretching the EC's thinking on infrastructures to its limits. However the discussions were amicable and positive, focusing on how an I3 proposal could be made to fit into the EC rules.

I think the general conclusion of our group was that one could construct a useful I3 proposal within the EC rules, and that a good proposal might be successful.

Volker Heine
Chairman, Psi-k Programme

4.2 Reports on ESF Workshops

4.2.1 Report on Euresco Conference Series: COMPUTATIONAL BIOPHYSICS: INTEGRATING THEORETICAL PHYSICS AND BIOLOGY

Euresco Conference
BIOPHYSICS FROM FIRST PRINCIPLES:
FROM THE ELECTRONIC TO THE MESOSCALE
San Feliu de Guixols - Spain
7-12 September 2002

Supported by the European Commission, Research DG, Human Potential Programme, High Level Scientific Conferences
(Contract No: HPCF-CT-2001-00032)

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

IBM

Generalitat de Catalunya

Organised by
Anne Chaka
NIST - Chemical and Physical Properties Division
Gaithersburg, USA

Flavio Seno
INFM and Dipartimento di Fisica Università di Padova, Padova, ITALY

The Euresco Conference "Biophysics from First Principles: From the Electronic to the Mesoscale" took place in San Feliu de Guixols from 7 to 12 September 2002. The Conference was the first of a series on "Computational Biophysics: Integrating Theoretical Physics and Biology" that will take place every two years.

The purpose of the conference was to bring together theoretical and experimental researchers from physics, chemistry, biological sciences and industry to foster interdisciplinary approaches to the study of living systems. 121 researchers from 28 countries spent five days discussing such innovative themes.

The conference primarily focused on the application of theoretical physics, from first principles to classical simulations, as well as statistical approaches, to understanding biological processes.

The Conference included the following sections:

-Understanding biological mechanisms

-Predicting biological activity of chemicals

-Molecular interactions and solvation: short and long range forces

-Structure and function of biological macromolecules

-Transition metal chemistry

The Programme of the Conference consisted of invited talks, contributed papers presented in oral form (13) or as a poster (two sessions for a total of 91 contributions). The quality of the discussion during the sessions was ensured by the chairpeople, who themselves are leading figures in the field.

The invited talks (one-hour long) were presented by 22 scientists: 5 from Germany, 4 from USA and Italy, 3 from Sweden, 2 from England, 1 from Austria, Israel, Spain and Switzerland. 20 minutes of each talk were devoted to questions and debate.

All the speakers tried to identify strengths and weakness of their particular reserach method(s) and to give opinions on promising new developments. This fact gave ample opportunity for extended and informal discussions during the scheduled afternoon free time and evenings.

One evening of the meeting was devoted to discuss the future of this series and to select the future chairpersons. It was decided that the title of series will change to "Biophysics from first principles: Integrating Theoretical Physics and Biology". The chairperson of the next meeting (2004) will be Ursula Roethilsberger (ETH-Zurich) and Paolo Carloni (SISSA-Trieste).

It was important that part of participants were PhD students and post docs from ab–initio group whose stay was partially supported by ESF.

The full list of participants and all abstracts are provided on the website

http://www.esf.org/euresco/02/pc02182

Anne Chaka (Gaithersburg) and Flavio Seno (Padova)

SCHEDULE

Saturday, September 7

Late afternoon/early evening REGISTRATION

19^{30} Dinner

21^{30} Get Toghether Drinks

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Sunday, September 8

8^{30}-8^{45} OPENING

A. Chaka and F. Seno

OVERVIEW

Chairmen: A. Lesk

8^{45}-9^{45} **M. Karplus** *(invited speaker)*

Department CCB, Harvard University, Cambridge, USA

Molecular Dynamics Simulation of Biomolecules: A perspective

9^{45}-10^{45} **C.M. Dobson** *(invited speaker)*

Department of Chemistry, University of Cambridge, UK

Protein Folding and Misfolding: From Theory to Therapy

10^{45}-11^{45} coffee break

11^{15}-12^{15} **M. Parrinello** *(invited speaker)*

Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

New approaches to the long timescale problem

12^{15}-12^{35} **M. Elstner**

Fachbereich Physik, Theoretische Pysik, University of Paderborn, Germany

QM/MM simulations of biomolecular structures and processes with an approximate DFT method

12^{35}-12^{55} **J. Shifman**

Division of Biology, California Institute of Technology, Pasadena, USA

Computational design of Calmodulin directed towards improving its binding specificity

13^{00} Lunch

PREDICTING BIOLOGICAL ACTIVITY OF CHEMICALS 1

Chairmen: S. Fischer

16^{00}-17^{00} **H. Kubinyi** *(invited speaker)*

University of Heidelberg and BASF AG, Ludwigshafen, Germany

Computer-Assisted Drug Design and Virtual Screening

17^{00}-17^{30} coffee break

17^{30}-18^{30} **P. Carloni** *(invited speaker)*

International School for Advanced Studies (SISSA/ISAS), Trieste, Italy

An ab initio Approach to Drug/Target Interactions

18^{30}-19^{30} **J. Rabinowitz** *(invited speaker)*

U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Research Triangle Park North Carolina, USA

The application of Computational molecular Methods to understand the Health Effects of Environmental Chemicals-Polycyclic Aromatic Hydrocarbons

19^{30} Dinner

21^{30}-23^{30} **POSTER SESSION I**

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Monday, September 9

STRUCTURE AND FUNCTION OF BIOLOGICAL MACROMOLECULES I

Chairmen: C. Molteni

8^{30}-9^{30} **K. Schulten** *(invited speaker)*

Department of Physics, University of Illinois at Urbana-Champaign, USA

Physics of photosynthetic units in purple bacteria: From light absorbtion to ATP synthesis

9^{30}-10^{30} **U. Roethilsberger** *(invited speaker)*

Laboratory of Inorganic Chemistry, ETH Zurich, Switzerland

Mixed Quantum/Classical Simulations of the Photoisomerization in Rhodopsin

10^{30}-11^{00} coffee break

11^{00}-12^{00} **W. Zinth** *(invited speaker)*

BioMolekulare Optik, Sektion Physik, Ludwig-Maximilians Universitaet Muenchen, Germany

Ultrafast spectroscopy of sub-nanosecond conformational dynamics of peptides

12^{00}-12^{20} **C. Clementi**

Department of Chemistry, Rice University, Houston, USA

Topology and Energetics in Protein Folding: Beyond the Go-like approach

12^{20}-12^{40} **N. Dokholyan**

Department of Biochemistry and Biophysics, University of North Carolina, Chapel Hill, USA

Expanding protein universe and its origin from the biological Big Bang

13^{00} Lunch

TRANSITION METAL CHEMISTRY

Chairmen: O. Eisenstein

17^{30}-18^{30} **P. Siegbahn** *(invited speaker)*

Department of Physics, Stockholm Univeristy, Sweden

Quantum Chemical Studies of Redox Active Enzymes

18^{30}-18^{50} **H. Schuessler**

Department of Physics, Texas A&M University, College Station, USA

Measurements of the cross-bridge attachment/detachment process within intact Sarcomeres by the surface plasmon resonance

18^{50}-19^{10} **J. S. Kuyucak**

Department of Theoretical Physics, Australian National University, Canberra, Australia

Structure-function relationships in ion channels from molecular and Brownian dynamics simulations

19^{30} Dinner

21^{30}-23^{30} **POSTER SESSION II**

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Tuesday, September 10

UNDERSTANDING BIOLOGICAL MECHANISMS

Chairmen: M. Scheffler

8^{30}-9^{30} **A. Warshel** *(invited speaker)*

Department of Chemistry, University of Southern California, Los Angeles, USA

Computer simulations of biophysical reactions: Balancing first principles and completeness

9^{30}-10^{30} **C. Micheletti** *(invited speaker)*

International School for Advanced Studies (SISSA/ISAS), Trieste, Italy

Emergence of protein-like secondary motifs from a geometrical variational principle

10^{30}-11^{00} coffee break

11^{00}-12^{00} **C. Rovira** *(invited speaker)*

Research Center on Theoretical Chemistry, Barcelona Scientific Park, Barcelona, Spain

Ligand Binding Properties of Hemeproteins Modeled by First Principles Molecular Dynamics

12^{00}-13^{00} **R. Car***(invited speaker)*

Department of Chemistry, Princeton University, Princeton, USA

First-principles simulations of biological systems: perspectives and challenges

13^{00} Lunch

Afternoon: Excursion to the Salvador Dali Museum

20^{00} Conference Dinner

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Wendsday, September 11

PREDICTING BIOLOGICAL ACTIVITY OF CHEMICALS II

Chairmen: W.A. Sokalski

8^{45}-9^{45} **D. Kleier** *(invited speaker)*

DuPont Crop Protection Products, Newark Delaware, USA

Computer-aided pesticided invention

9^{45}-10^{45} **M. Segall** *(invited speaker)*

University of Cambridge and ArQule (UK) Ltd., Cambridge, UK

Ab Initio Studies of Drug Metabolism

10^{45}-11^{15} coffee break

11^{15}-11^{35} **R.I. Dima**

Institute for Physical Science and Technology, Collega Park MD, USA

Surprising instabilities in prions: Evidence from NMR structures and sequence alignments

11^{35}-11^{55} **F. Di Rienzo**

INFM and Department of Chemistry, University of Modena and Reggio Emilia, Modena, Italy
Theoretical Investigations of electron transfer proteins: from biology towards bio-electronics.

BRIDGING LENGTH SCALES

Chairmen: W. Sokalski

11^{55}-12^{15}**P. Hunenberger**

Laboratorium fur Physikalische Chemie, ETH Zurich, Switzerland

Periodicity-induced artifacts in biomolecular simulations employing lattice-sum methods

12^{15}-12^{35} **A. Sevink**

Institute of Chemistry, University of Leiden, Leiden, The Netherlands

3D Mesoscopic Continuum Models for Organelles

12^{35}-12^{55} **G. Ayton**

University of Utah, Salt Lake City, USA

Interfacing molecular dynamics and macro-scale simulation for lipid bilayer vesicles

13^{00} Lunch

STRUCTURE AND FUNCTION OF BIOLOGICAL MOLECULES II

Chairmen: S. Cannistraro

16^{00}-17^{00} **R. Wade** *(invited speaker)*

Molecular and Cellular Modeling, European Media Laboratory, Heidelberg, Germany

Simulation-based Approaches to Protein Binding Kinetics

17^{00}-17^{30} coffee break

17^{30}-18^{30} **M.L. Klein** *(invited speaker)*

University of Pennsylvania, Philadelphia PA, USA

Computer Simulation Studies of Biomolecules at Soft Interfaces

18^{30}-19^{30} **H. Schrempf** *(invited speaker)*

Fachbereich Biologie/Chemie Abteilung Zoophysiologie, Universitat Osnabrueck, Osnabrueck, Germany

Biogenesis, recognition and degradation of the biopolymer chitin

19^{30} Dinner

21^{00} Special discussion on the future of this conference series

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Thursday, September 12

MOLECULAR INTERACTIONS AND SOLVATION: SHORT AND LONG-RANGE FORCES

Chairmen: J. Neugebauer

8^{30}-9^{30} **B.I. Lundqvist** *(invited speaker)*

Department of Applied Physics, Chalmers University of Technology, Goteborg, Sweden

Nonlocal-Correlation Density Functionals for Biophysics and Soft Matter

9^{30}-10^{30} **B. Kasemo** *(invited speaker)*

Department of Applied Physics, Chalmers University of Technology, Goteborg, Sweden

Vesicle to lipid bilayer transformation on solid surfaces; Monte Carlo simulations and recent experiments

10^{30}-11^{00} coffee break

11^{00}-12^{00} **A. Klamt** *(invited speaker)*

COSMOlogic GmbH&CoKG, Leverkusen, Germany

COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Physiological Partitioning

12^{00}-12^{20} **J. Ireta**

Theory Department, Fritz-Haber Institut der Max Planck Gesellschaft, Berlin, Germany

Hydrogen bond strength and the stability of the alpha -helix secondary structure of polypeptides: A DFT study

12^{20}-12^{40} **C. Rhodes**

Department of Physics, University of Illinois, Chicago, USA

Particle Mass Scale Proteomics

12^{40}-13^{00} Closing

13^{00} Lunch ==========

ABSTRACTS OF INVITED LECTURES

FIRST-PRINCIPLES SIMULATION OF BIOLOGICAL SYSTEMS: PERSPECTIVES AND CHALLENGES

Roberto Car

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AB INITIO APPROACH TO DRUG/TARGET INTERACTIONS

Paolo CARLONI

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We will present recent results from Car-Parrinello and hybrid Car-Parrinello/Molecular Mechanics simulations [1] of two enzymes target for pharmaceutical intervention, HIV-1 protease [2] and Caspase-3 [3]. We will focus on the reaction mechanism and on the interaction with inhibitors. We will conclude the talk by illustrating a possible use of first principle techniques for the investigation of the interaction between fraudulent substrates and the enzyme herpes simplex virus thymidine kinase [4].

[1] A. Laio, J. VandeVondele, U. Rothlisberger, *J. Chem. Phys.*, 2002, **116**, 6941-6947.

[2] The Role and Perspective of Ab-initio Molecular Dynamics in the Study of Biological Systems P. Carloni, U. Rothlisberger, M. Parrinello, *Acc. Chem. Res. 2002*, **35**, 455-464.

[3] Reaction Mechanism of Caspases: Insights from QM/MM Car-Parrinello Simulations, M. Sulpizi, A. Laio, J. VandeVondele, A. Cattaneo, U. Rothlisberger and P. Carloni, *Proteins*:SFG in press

[4] M. Sulpizi, P.Schelling, G.Folkers, P. Carloni, L. Scapozza, *J. Biol. Chem.* 2001, **76**:21692-7.

PROTEIN FOLDING AND MISFOLDING: FROM THEORY TO THERAPY

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Molecular self-assembly is an essential and universal characteristic of all living systems. The most fundamental of such processes is the folding of protein molecules into their functional states. There has been considerable progress in the last few years in understanding the underlying principles that govern this highly complex process. Central to much of this progress has been the development of ideas as to the nature of the energy surface or landscape for a folding reaction. These ideas have arisen from a combination of theoretical analysis and experimental investigation (Dinner et al., TIBS 25, 331-339, 2000). Of particular importance in the latter has been the concerted application of a wide range of experimental techniques, each able to describe aspects of the structural changes taking place during the folding process. NMR spectroscopy and protein engineering have both been key methods in this approach because of their ability to provide structural and dynamical information at the level of individual residues. Recently, new approaches have been devised that combine experimental data directly with simulation techniques to define the structures of key species on the folding surface (Vendruscolo et al., Nature 409, 641-645, 2001).

Recently, much research has also focused on the realisation that proteins can misfold in vivo and that this phenomenon is linked with a wide range of diseases. We have been investigating in particular the nature of the amyloidogenic conditions (that include Alzheimers disease and the spongiform encephalopathies, e.g. BSE and CJD) in which protein misfolding leads to the aggregation of proteins, often into fibrillar or thread-like structures. We have looked in detail at a non-neuropathic amyloidosis associated with lysozyme, one of our model systems for investigating the fundamentals of protein folding. (Booth et al., Nature 385, 787-793, 1997; Canet et al., Nature Struct. Biol. 9, 308-315, 2002). This work has recently been extended by the finding that many proteins not associated with clinical manifestations of disease can form amyloid structures in the laboratory under appropriately chosen conditions (Chiti et al., PNAS 96, 3590-3594, 1999; Fandrich et al., Nature 410, 165-166, 2001). Such findings have led us to explore some of the underlying characteristics of protein sequences that result in a high propensity to form amyloid structures (Chiti et al., Nature Struct. Biol. 9, 137-143, 2002), and to put forward ideas concerning the fundamental origin of the various diseases associated with the formation of such species (Bucciantini et al., Nature 416, 507-511, 2002). We have also speculated more generally that the avoidance of aggregation could be a significant driving force in the evolution of protein sequences and structures (Dobson, Phil. Trans. R. Soc. Lond. B356, 133-145, 2001; Dobson, Nature in press).

MOLECULAR DYNAMICS SIMULATIONS OF BIOMOLECULES: A PERSPECTIVE

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VESICLE TO LIPIDE BILAYER TRANSFORMATION ON SOLID SURFACES; MONTE CARLO SIMULATIONS AND RECENT EXPERIMENTS

Benght Kasemo

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COSMO-RS: FROM QUANTUM CHEMISTRY TO FLUID PHASE THERMODYNAMICS AND PHYSIOLOGICAL PARTITIONING

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Continuum solvation models like COSMO (Conductor-like Screening Model) have proven to be very efficient and reliable tools for the approximate treatment of solvents in quantum chemical calculations. The combination of density functional theory with such continuum models turns out to give good qualitative results at moderate computation time, allowing molecules up to 50 atoms being handled on standard workstations or even PCs within hours or days. But, despite of the good results, which can be achieved by such methods for solutes in some solvents, e.g. in water and in alkanes, they are not capable of a general quantitative description of solutes in solvents and in mixtures, as it is usually required in many situations, especially in chemical engineering thermodynamics.

A perfectly novel access to the problem is provided by the COSMO-RS method. This uses the output of COSMO calculations, i.e. energies and screening charge densities on the molecular surface, as basis for a statistical thermodynamics treatment in which the interactions of molecular surfaces, which occur in liqid systems, are described as pair-wise interactions of molecular surface pieces, and the interaction energies are functions of the two screening charge densities on the pieces in contact. Hence the necessary information for the interaction energies arises from the quantum chemical calculations. In combination with a fast, but exact(!) statistical thermodynamics for the interacting surface pieces COSMO-RS provides an efficient new technique for the calculation of solubilities, partition coefficients and general fluid phase equilibria.

This new method is much more efficient and probably more accurate than MD- or MC-simulations which are used for liquid systems by many computational chemists. In addition it provides more physical insight into the problem of solvation. On the other hand it is much more general applicable than group contribution methods like CLOGP or UNIFAC, which is state of the art in chemical engineering.

Based on DFT/COSMO calculations COSMO-RS has been parameterised for elements H, C, N, O, F, Cl, P, S, Br, and I, yielding remarkable accuracy for vapor pressures, ΔG_{hydr} and partition coefficients. Even more, solubilities, miscibilities, and phase diagrams are well described.

For the use in biophysics and medicinal chemistry such direct property calculations may be of considerable value. All properties are calculated by surface integrals and hence logarithmic partition coefficients and hydration energies can be visualised on the molecular surface. The ability to calculate solubility of drug-like compounds is of special importance. In addition, COSMO-RS offers a set of linear descriptors for arbitrary partition behaviour, which may be of

great use in any QSAR study which has to do with more complicated partition problems like blood-brain, intestinal absorption, BCF, etc. An outlook will be given to application to large molecules and to docking questions, based on an semi-empirical COSMO-RS parameterisation, combined with linear scaling semi-empirical codes. Fast shortcuts of COSMO-RS, which may be useful for HTS-studies will be discussed as well.

COMPUTER-AIDED PESTICIDE INVENTION

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Computer modeling can aid in the invention of compounds that are not only capable of beneficial action at a target site, but also capable of movement to that target site following remote application. Pest control is not in the applied dose, but rather in the dose delivered at a site critical to the survival of the pest. Biophysical processes that influence delivery include permeation of biological membranes, transport through the vascular system, chemical degradation at the site of application, and metabolism enroute to the site of action. Computer modeling and simulation can be an aid in understanding these processes, and in the design of compounds that can overcome limitations imposed by them. Models useful for the invention of pesticides can be built either from a fundamental understanding of the biophysical processes involved in controlling the pest or from collections of data that relate biological efficacy to chemical structure. For complex systems semi-empirical methods based on first principles, but parameterized against experimental data often offer the best approach.

In this talk, we will discuss the development of semi-empirical models that describe the absorption and distribution of pesticides within pest and host organisms. Example applications of these models to the design of pesticides that overcome barriers to adsorption, and distribution will also be discussed. We will also describe how unsuitable reactivity of pesticides can be understood and corrected using both first principle and empirical models of the degradation processes involved. Illustrations will be drawn from applications of semi-empirical electronic structure theory to the design of pesticides with improved photostability, and of data mining techniques to the identification of structural features that presage conjugation with ubiquitous reactive groups present in the environment.

Given the right data, empirical modeling can provide useful forecasts of desired molecular behavior without explicitly accounting for the underlying biophysical processes involved in expressing the behavior. In our experience, even low-resolution screening data can be used to develop classification schemes that are valuable in forecasting pest control from chemical structure. As an added benefit, if the descriptors used to build the empirical models are readily interpretable, the models may elucidate the underlying biophysical processes.

COMPUTER SIMULATION STUDIES OF BIOMOLECULE AT SOFT INTERFACES

Michael L. Klein

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The talk will review the simulation methods currently available for modeling the behaviour of biomolecules at soft interfaces. Particular attention will be given to the problem of spanning the length and time scales needed to explore phenomena that are relevant for the interaction of peptides and peptide-mimics with phospholipid bilayers.

COMPUTER-ASSISTED DRUG DESIGN AND VIRTUAL SCREENING

Hugo Kubinyi

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With the ongoing progress in protein crystallography, rational approaches in drug design become more and more important. The first success story in structure-based design was the antihypertensive drug Captopril, an Angiotensin-converting enzyme (ACE) inhibitor. Another impressive example of a structure-based, computer-assisted design is the anti-flu drug Zanamivir, which resulted from an inspection of the 3D structure of neuraminidase with the computer program GRID. Several examples of the structure-based design of marketed drugs and drug candidates being in clinical development illustrate the potential of such approaches.

Whereas structure-based design can be regarded as the predominant strategy of the last decade, several computer-assisted methods were developed more recently. If thousands of candidates and even larger structural databases shall be tested whether they are suited to be ligands of a certain binding site, this cannot any longer be done by hand. The design process has to be automated, i.e. performed with the help of the computer. Two methods for this purpose are the computer programs CAVEAT and LUDI. CAVEAT uses the 3D information of a ligand, e.g. a peptide, in its receptor-bound conformation to design conformationally restricted small molecules, having the same geometry of interacting side chains. The de novo design program LUDI, developed by Hans-Joachim Bhm at BASF in the early 1990s, was a significant improvement over the early prototypes DOCK and GROW. The program automatically identifies hydrogen bond donor and acceptor sites, as well as aliphatic and aromatic hydrophobic areas of this part of the protein surface. In the next step, LUDI attributes interaction sites and searches any database of 3D structures of small and medium-sized molecules for potential ligands. Fitting candidates are prioritized by a simple but efficient scoring function. In a last step, the program is capable to attach groups, fragments and/or rings to a hit or to an already existing lead structure.

Combinatorial chemistry added a new dimension to drug design, in significantly speeding up the synthesis of potential new drug candidates; diversity and drug-likeness are important criteria for the design of combinatorial libraries. An interesting approach to determine the drug-likeness of series of organic molecules has been developed by Jens Sadowski at BASF. Simple structural parameters and scoring values of 0 and 1 were used to train a neural net with sets of chemicals, e.g. from the Available Chemicals Directory, and drugs, e.g. from the World Drug Index. The discrimination of the training sets as well as the predictions for the rest of the huge databases are

in the range of 75-80%. The method allows a reasonable ranking and enrichment of promising candidates in large in-house, external, combinatorial, and virtual libraries. In this manner, financial resources are focused to sets of compounds of general biological interest.

Further progress in rational drug design is to be expected from the SAR by NMR method, from the combinatorial construction of new ligands, and from flexible docking approaches, like the computer program FlexX. SAR by NMR (structure-activity relationships by nuclear magnetic resonance), recently developed by Stephen Fesik at Abbott, allows the construction of high-affinity ligands from small molecules with much lower affinities. Libraries of typically thousand small molecules are screened against a certain protein. If two small molecules bind to different but adjacent sites of the protein, both ligands are connected by an appropriate linker. In this manner, high-affinity ligands result within short time.

Several other techniques have been developed, e.g. the dynamic assembly of ligands and the click chemistry approach. In all cases, high-affinity ligands are constructed from low-affinity, smaller ligands. Such experimental techniques are supported by programs for flexible docking. A highly efficient and extremely fast program for the incremental docking of ligands into their binding site, FlexX, was developed by Thomas Lengauer and Matthias Rarey, Institute for Algorithms and Scientific Computing of GMD, Bonn, in cooperation with BASF. FlexX starts by dissecting a ligand into rigid fragments. One or several different base fragments are selected and positioned in favorable orientations within the binding site. Fragments are added, step by step, using a tree-search technique for placing the ligand incrementally into the binding site. Only low energy conformations are created and the different results are ranked according to favorable interaction energies, using the scoring function of the de novo design program LUDI.

Further extensions of this program include the combinatorial design of ligands from series of building blocks. Also several other institutions and pharmaceutical companies are going to develop such dedicated computer programs for the structure-based design of ligands from selected building blocks, by combinatorial docking. In this manner, out of a virtual library of billions of possible ligands only those are selected that smoothly fit the binding site, in geometry as well as in their properties.

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[6] T. Mitchell and G. A. Showell, Design strategies for building drug-like chemical libraries, *Curr. Opin. Drug Disc. Dev.* **4**, 314-318 (2001).

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NONLOCAL-CORRELATION DENSITY FUNCTIONALS FOR BIOPHYSICS AND SOFT MATTER

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For structure, bonding, and other properties of biophysical and soft-matter systems there is a challenge for quantum mechanics to account for both strong local atom bonds and weak nonlocal van der Waals (vdW) interactions between atoms separated by empty space. A recently proposed scheme within the Density Functional Theory (DFT) is described and applied to some pilot systems. It provides a basis for systematic improvements beyond the local- (LDA) and semilocal-density approximations (GGA), to incorporate medium- and long-ranged correlations, including the vdW forces. Utilizing, e.g., planar, cylindrical, and spherical symmetries simplifies the necessary reduction of the adiabatic connection formula. With their planar geometry, graphitic materials are ideal examples of such systems, having both very strong bonds in the planes and weak vdW forces between them. Here our new density functional (DF), which encompasses nonlocal correlations among the electrons, is applied successfully to obtain structure, bonding, and compressibility in good agreement with experiment. Ongoing DF development for general geometry is also described, where the nonlocal correlations are expressed in terms of a density-density-interaction formula, whose dependence on density and distance have a form that allows rapid numerical evaluation.

EMERGENCE OF PROTEIN-LIKE SECONDARY MOTIFS FROM A GEOMETRICAL VARIATIONAL PRINCIPLE

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Optimal geometrical arrangements, such as the stacking of atoms, are of relevance in diverse disciplines [1]. A classic problem is the determination of the optimal arrangement of spheres in three dimensions in order to achieve the highest packing fraction; only recently has it been proved [1] that the answer for infinite systems is a face-centred-cubic lattice. This simply stated problem has had a profound impact in many areas ranging from the crystallization and melting of atomic systems, to optimal packing of objects and subdivision of space. Here we study an analogous problem–that of determining the optimal shapes of closely packed compact strings. This problem is a mathematical idealization of situations commonly encountered in biology, chemistry and physics, involving the optimal structure of folded polymeric chains. The problem is tackled by a stochastic optimization techniques which exploits ideas developed recently in the context of ideal knot shapes[2]. In particular, for a fixed confining boundary (a box, or upper limit to radius of gyration) we search for the (discretised) centerlines of the thickest tube that can be accomodated. The maximum thickness can be limited by local tight bends or by the close approach of distant parts of the tube. We find that, in cases where boundary effects are not dominant, helices with a particular pitch-radius ratio are selected. Strikingly, the same ratio (to within 1%) is observed in helices in naturally-occurring proteins[3]. It is also shown, that, to the same accuracy also the double helix of DNA satisfy an analogous optimal criterion[4].

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NEW APPROACHES TO THE LONG TIMESCALE PROBLEM

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The free energy surface of a complex system is usually characterized by the presence of deep minima separated by large barriers. Such minima correspond to distinct states of the system, and transitions among these minima reflect important changes such as chemical reactions or conformational modifications. Direct simulation of these processes is frustrated by the exponential dependence of the rate on the barrier height, and simulations often do not leave the free energy minimum from which they were started. In order to solve this problem we develop a two-pronged strategy. On the one hand we define a variational procedure that, once the initial and final states are known, is able to reconstruct the real dynamical trajectory connecting these two points [1]. On the other we introduce a coarse-grained non-Markovian dynamics that can reconstruct the free energy dependence on a set of suitably defined collective coordinates [2]. The synergetic effect of these two methods goes a long way towards alleviating the time scale problem of molecular dynamics simulations.

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THE APPLICATION OF COMPUTATIONAL MOLECULAR METHODS TO UNDERSTAND THE HEALTH EFFECTS OF ENVIRONMENTAL CHEMICALS-POLYCYCLIC AROMATIC HYDROCARBONS

James Rabinowitz, Stephen B. Little and K. Brown

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In evaluating the risk posed by chemicals introduced into the environment, information about their molecular mechanism of action provides a basis for extrapolating from the laboratory to the environment. Polycyclic aromatic hydrocarbons (PAH) are a large class of anthropogenic chemicals found in a number of environmental circumstances. Some class members are potent mutagens and animal carcinogens while other class members show little similar activity after considerable testing. Benzo[a]pyrene (BaP) is a class member that has been identified as a carcinogen. The features of its structure that might confer this activity were identified and studied by a number of different methods. A metabolite, the bay region diol epoxide, was identified as the ultimate carcinogen and its structure and reactivity studied by molecular modeling methods. When considering a series of bay region diolepoxides, it was found that molecules with a crowded bay region have a different pattern of interaction with DNA than molecules with a simple bay region. The PAHs with a crowded bay region were often found to be more potent mutagens and carcinogens. These PAHs and their diol epoxides were also shown to be nonplanar. The relationship between bay region crowding, nonplanarity and reactivity will be discussed. The interaction of PAHs and their metabolites with the estrogen receptor will also be discussed in consideration of possible mechanisms of action for additional environmental effects. (This work does not necessarily reflect EPA policy)

MIXED QUANTUM/CLASSICAL SIMULATIONS OF THE PHOTOISOMERIZATION IN RHODOPSIN

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LIGAND BINDING PROPERTIES OF HEMEPROTEINS MODELED BY FIRST PRINCIPLES MOLECULAR DYNAMICS

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A quantitative study of the properties of the myoglobin active center and its interaction with O2, CO, and NO, by means of Car-Parrinello molecular dynamics, will be performed. The dynamical motion of the ligands and its preferential conformations will also be analyzed: while the CO ligand undergoes an essentially harmonic dynamics around its linear equilibrium position, the O2 ligand prefers a conformation where the O-O axis projection on the porphyrin plane bisects one of the porphyrin quadrants. However, it "jumps" from one porphyrin quadrant to another one every 4 - 6 ps [1]. Finally, a combined QM/MM methodology will be used to investigate the heme-protein interaction. Further aspects of the binding of ligands in other hemeproteins will also be discussed.

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BIOGENESIS, RECOGNITION AND DEGRADATION OF THE BIOPOLYMER CHITIN

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Chitin is a linear polymer consisting of N-acetylglucosamine residues which can associate in a parallel (b) or an antiparallel fashion (a). Naturally occurring chitin types vary in the length of their chains, the degree of crystallinity and the presence of accessory compounds. In consequence the consistency of the chitinous layers in different organisms, such as arthropods, molluscs, nematodes, worms and fungi, varies. Chitin synthesis depends on chitin synthetases, the genes of which have been identified within yeast, fungi and insects. Upon deacetylation of chitin, chitosan is formed which is a component of the cell wall of fungi.

Streptomycetes secrete small proteins (CHBs) which effectively target chitin-containing organisms. CHBs act like a glue, therefore streptomycetes closely associate with the chitin-containing organisms. CHB1 contains 201 amino acids with four tryptophan residues, three of which are buried, one is exposed. Specific targeting of a-chitin by CHB1 is mainly dependent on this exposed residue and the presence of S-S bridges. The low resolution structure of CHB1 is made up of one elongated main globule (4 x 3.5 nm) and a protuberance of 2 nm in width. The homologues of CHB1 differ in their dissociation constant and their specificity of recognition; they have been found among several different chitinolytic bacteria.

The large repertoire of chitinases facilitates degradation of chitin and chitin-containing organisms by streptomycetes. The corresponding degradation products are specifically taken up and utilized as C- and N-source. Moreover streptomycetes are able to secrete small antifungal proteins and inhibitors of chitin synthetases and thus play a part in biocontrol in the soil .

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PHYSICS OF PHOTOSYNTHETIC UNITS IN PURPLE BACTERIA: FROM LIGHT ABSORBTION TO ATP SYNTHESIS

Klaus Schulten

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This lecture will demonstrate how computational methods in biology support and complement observation as well as integrate physical descriptions from the electronic to the multi-protein level. It will focus on purple bacteria that fuel their metabolism with light energy and have developed for this purpose an efficient apparatus for harvesting sunlight, the photosynthetic unit (PSU). The atomic structure of all PSU components, minimally four protein complexes, have been solved. The components work together to absorb light, use its energy to charge a membrane, first through electrons and then through protons, and with the charge drive the synthesis of ATP. Our group has modeled in situ all individual protein components of the PSU, beginning with the light harvesting proteins, a scaffold for hierarchical aggregates of chlorophylls and carotenoids, that absorb sun light, convert it within a few hundred femtoseconds to excitonic excitation that migrates within about 50 ps to the center of the overall structure where it fuels an electron transfer process charging the membrane. We discuss how a still ongoing analysis wrestled from an atomic level structure an explanation of the high degree of efficiency of the energy migration based on electronic coupling between the chlorophyll and carotenoid constituents.

Biological cells function at physiological temperatures, despite the respective thermal disorder, and also because of it. This poses the challenge to measure and understand the role of thermal disorder, in particular, for bioelectronic systems governed by quantum physics. The lecture describes stochastic quantum mechanics as observed and measured for photosynthetic systems in single molecule as well as exciton optical spectra of light harvesting proteins and in electron transfer.

We finally outline ongoing research that seeks to explain how, in a compact molecular apparatus, electron-hole separation across the membrane is converted by a the bc1 protein complex into a trans-membrane protein gradient, and how this gradient is converted by ATP synthase first into mechanical energy and then into synthesis of ATP.

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AB INITIO STUDIES OF DRUG METABOLISM

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The Cytochromes P450 (P450s) are a superfamily of enzymes responsible for the metabolism of a wide range of xenobiotic molecules. A challenge for drug design is to ensure that the molecule has an appropriate stability with respect to metabolism by P450s and that the metabolites produced (if any) are non-toxic.

The quantitative in silico prediction of drug metabolism by Cytochrome P450s requires an understanding of the catalytic mechanism at a molecular level. Computational experiments, based on calculations using the plane wave density functional theory approach, have been used probe the detailed reaction mechanism of P450s.

A P450 enzyme contains several thousand atoms, well beyond the largest system size that can currently be studied using first principles quantum mechanical simulations. Therefore, the most important components of the active site must be studied independently from the surrounding protein structure, or embedded in a classical model of the protein environment.

The broad specificity and regioselectivity of P450 enzymes means that the electronic structure of substrate molecules plays an important role in determining sites of metabolism. Ab initio methods can be used to identify the properties that will predict the vulnerability of sites on a molecule to metabolism by P450.

In practice, ab initio methods are too computationally expensive to be used in a high-throughput predictive model. However, in combination with experimental results, ab initio calculations can be used to parameterise models based on semi-empirical quantum mechanical approaches. In trials, the electronic model alone could explain $> 65\%$ of the observed sites of metabolism due to the P450 enzyme CYP3A4. When a model of the steric influences of the active site was included, this improved to $> 80\%$.

Ultimately, the goal is to develop a model that can predict the rate of metabolism from the compound structure. This will require prediction of the affinity of a compound for the active site, rates of reduction of the enzyme-substrate complex and rates of alternative decoupling pathways that limit the efficiency of metabolism. Not all of these can be approached using ab initio methods. However, a number of these mechanisms present opportunities for further first principles investigations.

QUANTUM CHEMICAL STUDIES OF REDOX-ACTIVE ENZYMES

Per Sieghban

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For the past five years our group has been working on mechanisms for enzymes containing active sites with transition metals. Some of the most interesting enzymes can be found in this group such as, for example, photosystem II, cytochrome oxidase, methane monooxygenase, ribonucleotide reductase, methylcoenzyme M reductase, nitrogenases, hydrogenases and catalases. In

the studies of these enzymes the hybrid DFT method B3LYP has been used and the active site has usually been modeled by the metal complex including its first shell amino acid ligands only. Examples of the accuracy of the present approach will be given for manganese catalase. The rest of the talk will focus on two recent studies, the first one on methylcoenzyme M reductase where a larger model than previously has been used (107 atoms) and for which a new mechanism, where a free methyl radical appears, is suggested. The second study is on a comparison of dioxygen cleavage for ribonucleotide reductase and methane monooxygenase. An electron transfer in ribonucleotide reductase is suggested to explain the difference in rates. It was found important to optimize the geometry including a surrounding dielectric medium.

SIMULATION-BASED APPROACHES TO PROTEIN BINDING KINETICS

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I will describe the application of Brownian and molecular dynamics simulation techniques to study protein-ligand binding and unbinding, focusing on examples of protein-protein[1], enzyme-substrate[2] and enzyme-inhibitor complexation. The roles of electrostatic interactions and protein motions in these binding events will be discussed, along with implications for binding specificity and structure-based drug design.

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COMPUTER SIMULATIONS OF BIOPHYSICAL REACTIONS : BALANCING FIRST PRINCIPLES WITH COMPLETENESS

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Simulations of key types of biophysical reactions are outlined , considering very fast photobiological reactions, enzymatic reactions and the action of ion channels[1]. It is argued that a proper simulation strategy must allow one to study the relevant biophysical features in the available computer time. Thus, it may be unwise to use approaches that look formally very rigorous but are unable to explore the energetics of the complete system or to properly address the biologically relevant issues. Some examples are given, showing that high level ab initio approaches might not give high level biological information. The issue of the proper balance between the requirement of rigorous treatments and the available computer power is also addressed.

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ULTRAFAST SPECTROSCOPY OF SUB-NANOSECOND CONFORMATIONAL DYNAMICS OF PEPTIDES

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Ultrafast spectroscopy on the femtosecond time scale has revealed the molecular mechanisms of many reactions in photobiology. These time resolved experiments yield important information for the understanding of fast processes, such as the photosynthetic energy and electron transfer, the primary reactions of vision and the initiation of the proton transfer in retinal proteins. In the present paper we will apply time resolved spectroscopy to the study of the fastest structural changes in peptids. By this way we hope to obtain a better understanding of the elementary steps in protein folding.

We introduce a novel approach to allow femtosecond time resolution for the study of peptide structural dynamics: we use a photo-switchable peptide, where the peptide chain is cyclized via an optical trigger molecule. A modified azobenzene molecule has been chosen as optical trigger, since azobenzene dyes are known to photoisomerize within fractions of picoseconds at high quantum yields and to induce significant changes in geometry. Femtosecond time-resolved spectroscopy on these model-peptides is combined with computer simulation of the light-triggered motions. This combination offers an attractive integrated approach towards the understanding of peptide conformational dynamics.

Time resolved spectroscopy exhibits fast absorption transients describing reactions of the chromophore and its surrounding. They indicate that the cis to trans isomerization of the azobenzene is finished within 1 ps. Subsequent absorption transients can be assigned to the relaxation of excess vibrational energy out of the molecule. On the 10 - 100 ps time scale we observe changes of the strain between the chromophore and the peptide chain. In this time range the sub-nanosecond conformational relaxation of the peptide is visible via the chromophore absorption. The photochemical cis/trans-isomerization of the chromophore and the resulting peptide relaxations have been simulated with molecular dynamics calculations. The calculated reaction kinetics, as monitored by the energy content of the peptide, were found to match the spectroscopic data. Thus we verify that peptide structural changes can occur on the picosecond time scale and that all-atom molecular dynamics simulations can quantitatively describe the sub-nanosecond conformational dynamics, strengthening the confidence in corresponding predictions for longer time-scales.

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INTERFACING MOLECULAR DYNAMICS AND MACRO-SCALE SIMULATION FOR LIPID BILAYER VESICLES

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A continuum-level model for a Giant Unilamellar Vesicle (GUV) is bridged to a corresponding atomistic model of a DMPC bilayer at various cholesterol concentrations via computation of the bulk modulus. The bulk modulus, along with other microscopically determined parameters, are passed to a continuum-level model operating in time and length-scales orders of magnitude beyond that which is accessible by atomistic-level simulation. The continuum-level simulation method employed is the Material Point Method (MPM), and the particular variation used here takes advantage of the spherical nature of many GUV's. An osmotic pressure gradient due to a solvent concentration change is incorporated into the continuum-level simulation, resulting in osmotic swelling of the vesicle. The model is then extended to treat mixtures of DMPC and cholesterol, where small domains of different composition are considered.

TOPOLOGY AND ENERGETICS IN PROTEIN FOLDING: BEYOND THE GO-LIKE APPROACH

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Recent experimental results suggest that the native fold, or topology, plays a primary role in determining the structure of the transition state ensemble. Starting from these observations, several simple theoretical models have been developed in order to exploit the topological information of the native structure to make predictions about the folding mechanism of real proteins. Although the central role of native state topology in determining the folding mechanism is thought to be a quite general result–at least for small two-state folding proteins– there are remarkable exceptions. Recent experimental findings show that topology alone can not always and completely determine the folding mechanism and demonstrate that the balance between topology and energetics in the folding of proteins is very delicate. It is clear from these observations that there is the need for a better understanding of the interplay between topology and energetics in protein folding in order to make significant progress and to be able to make quantitative predictions. We discuss how is possible to study and account for the role of energetical heterogeneity, energetic frustration, side-chain and steric effect, and we present the results from a first investigation in this direction.

THEORETICAL INVESTIGATIONS OF ELECTRON TRANSFER PROTEINS: FROM BIOLOGY TOWARDS BIO-ELECTRONICS

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The exploitation of biological systems and mechanisms for the realisation of electronic devices based on biomolecules is a key challenge of the current research in nanoelectronics. In this perspective, the use of electron-transfer proteins is particularly attractive because of their natural redox properties and their self-assembly capabilities. The possibility of eliciting current through the redox states of azurin, a copper-containing electron transfer protein, has been demonstrated with scanning tunneling microscopy techniques (STM) [1]. Furthermore, a few working solid state prototype devices, which function as rectifiers, have been recently built exploiting azurin layers as semiconductor materials [2]. A fundamental issue is therefore to understand which are the electronic and structural features of azurin that allow the devices to work as rectifiers. In this paper, the application of both ab-initio theoretical modelling and classical simulation techniques is discussed as a mean to directly address these basic problems. First, the focus is on the active site of the protein, which is formed by the Cu ion and its five amino acid ligands. This site is studied both in its reduced (Cu(I)) and oxidized (Cu(II)) forms, starting directly from the experimental X-ray structures available, to characterise the electron states of the system and get new insights on its redox properties, which seem to be determining for current flux in the devices. We discuss here the results of Density Functional Theory (DFT) calculations in the Car-Parrinello approach, performed with plane wave pseudopotentials to model the electron-ion interactions. The whole protein structure is also taken into account in order to point out whether its structural and surface properties can affect the device performances. In particular, the Molecular Electrostatic Potential (MEP) and the dipolar features of azurin, computed with force field based methods [3,4], appear to be relevant for understanding the rectifying behaviour shown by the devices.

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SURPRISING INSTABILITIES IN PRIONS : EVIDENCE FROM NMR STRUCTURES AND SEQUENCE ALIGNMENTS

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Prion proteins are associated with neurodegenerative diseases induced by transmissible spongiform encephalopathies. The most spectacular event in the formation of the infectious (scrapie) form is the conformational change from the predominantly alpha-helical state of the normal cellular prion protein to the scrapie state that is rich in beta-sheet. Using sequence alignments and structural analysis of the available NMR structures of the cellular prion we explore the propensities of its helices to be in a beta-strand conformation. Comparison of a number of structural characteristics (such as solvent accessible area, distribution of dihedral angles, nature of residues in local and non-local contacts, distribution of regular densities of amino acids, clustering of hydrophobic and hydrophilic residues in helices) between the structures of the cellular form of prions and a databank of "normal" proteins shows that the most unusual features are found in helix 2 (residues 172-194). Our analysis shows that, in addition to the previously proposed role for the segment (90-120) and possibly H1, the C-terminus of H2 and possibly N-terminus may play a role in the alpha to beta transition.

This suggests that the instability of normal prion protein proteins may play a role in their being susceptible to the profound conformational change.

PARTICLE MASS SCALE PROTEOMICS

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A physically anchored cryptographic approach to the theoretical organization of the particle mass scale leads to an optimized hierarchical structure whose group architecture is strikingly congruent with the archetype prevalent in the living world, particularly that observed in patterns of taxonomic and proteomic organization. Since the system of classification for the physical particle states is expressed in precise mathematical relations, the existence of this correspondence suggests that the identical mathematical procedures could potentially be adapted to provide a powerful new organizing principle for an enormous volume of biological data that would facilitate drug discovery and accelerate important applications in the clinical arena. The cryptographic/biological parallel can be pictured through an array of correspondences which culminates in the portrayal of the physical particle masses as the counterparts of the biological gene products, the proteins. Accordingly, this analogy presents a statement of direct correspondence between (a) the pattern represented by the network of particle interactions and (b) the

analogous systematics of proteomic regulation. This concept will be discussed by comparing the pattern of properties and reactions exhibited by physical particle states with the model furnished by the recent analysis of the yeast proteome.

EXPANDING PROTEIN UNIVERSE AND ITS ORIGIN FROM THE BIOLOGICAL BIG BANG

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The bottom up approach to understanding the evolution of organisms is by studying molecular evolution. With the large number of protein structures identified in the past decades, we discover peculiar patterns that nature imprints on protein structural space in the course of evolution. In particular, we discover that the universe of protein structures is organized hierarchically into a scale-free network. We develop a model based on known mutation mechanisms that explains the cause of these patterns from the perspective of the divergent evolution scenario.

QM/MM SIMULATIONS OF BIOMOLECULAR STRUCTURES AND PROCESSES WITH AN APPROXIMATE DFT METHOD

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Although density functional theory (DFT) has been shown to be very reliable and efficient for chemical and biophysical applications, many biomolecular problems of interest present still a considerable challenge for its routine application due to computer time limits (also in a QM/MM framework). This concerns system sizes with more than about 100 atoms on the one hand, on the other hand problems, where extensive MD or MC sampling is desirable. Further, often the evaluation of many structures (i.e. by calculating reaction pathways) is necessary, thereby easily exceeding available computational resources. In the view of these requirements, we have developed an approximation to DFT, which is considerably more efficient by trying to sustain the reliabiliy of DFT. Since DFT lacks the description of dispersion forces, which is inherited by the approximate DFT method, we have included them empirically because of their crucial role for the stability of protein and DNA structures. The method has been implemented into QM/MM and linear scaling algorithms, and we present investigations of the stability and dynamics of polypeptides, especially a MD simulation of the crambin molecule (650 atoms treated with QM) in solution over 0.35 ns (a similar simulation has been performed for a DNA dodecamer in water solution). We further have studied proton transfer reactions in different systems like Bacteriorhodopsin and bacterial reaction center. Here, the computational efficiency allows to

generate minimum energy paths (MEP) and to perform potential of mean force calculations along these pathways. The scheme has also been extended for the treatment of excited states via time-dependent DFT and for non-adiabatic dynamics algorithms to study high energy collisions, light-matter interactions (inclusion of electromagnetic field in the Hamiltonian) and photochemical events.

PERIODICITY-INDUCED ARTIFACTS IN BIOMOLECULAR SIMULATIONS EMPLOYING LATTICE-SUM METHODS

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Ewald and related mesh methods (P3M,PME) are nowadays routinely used in explicit-solvent simulations of solvated biomolecules, although they impose an artificial periodicity on systems which are inherently non-periodic. Our strategy to investigate the nature and magnitude of possible periodicity-induced artifacts is to use continuum electrostatics, with the goal of understanding, correcting, and ultimately eliminating finite-size effects. This approach will be illustrated in the context of three case studies: (i) the conformational equilibrium of a polyalanine octapeptide (charged termini; no counter-ions), (ii) simulations of a small protein (ISL-1, overall charge +11e; with or without counter-ions), and (iii) simulations of a DNA duplex (dodecamer, overall charge -22e; with or without counter-ions). It is found that periodicity-induced artifacts can significantly affect the conformational equilibria of biomolecules in simulations (sometimes in a predictible way), and that these effects can be reduced by the inclusion of a neutralizing amount of counter-ions.

HYDROGEN BOND STRENGTH AND THE STABILITY OF THE ALPHA-HELIX SECONDARY STRUCTURE OF POLYPEPTIDES: A DFT STUDY.

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The alpha-helix is the prominent "secondary structure" in protein conformations. It is stabilized by hydrogen bonds (hb). Despite the paramount importance of the alpha-helix formation and stability for a healthy function of proteins, a careful analysis of the nature and strength of the hb in alpha-helix conformations of different lengths is still lacking. In this work we address this question by performing density functional theory calculations on finite (from 1 up to 19 peptide units) and infinite polyalanine and polyglycine chains. The calculations have been performed

using different density gradient corrected functionals (BLYP and PBE) and a hybrid functional (B3LYP). First, we will present a procedure to estimate the hb strength on a helical chain taking fully into account the helix back bone. Using this procedure we find an unexpectedly large cooperativity between hbs in an alpha-helix: Compared to an isolated hb the energy per hb in an infinite helix is strengthened by a factor of two. Further, using the same procedure we have studied the relation between hb strength and uniaxial strain. Our results show that the hb energy decreases with increasing strain and eventually the helix becomes thermodynamically unstable and undergoes a first order phase transition.

STRUCTURE-FUNCTION RELATIONSHIPS IN ION CHANNELS FROM MOLECULAR AND BROWNIAN DYNAMICS SIMULATIONS

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Ion channels are formed by specific proteins embedded in the cell membrane and provide pathways for fast and controlled flow of ions down the electrochemical gradient. This activity generates action potentials in nerves, muscles and other excitable cells, and forms the basis of all movement, sensation and thought processes in living beings. While the functional properties of ion channels are well known from physiological studies, lack of structural knowledge has hindered development of theoretical models necessary for understanding and interpretation of these properties. Recent determination of the molecular structures of potassium and mechanosensitive channels from x-ray crystallography has finally broken this impasse, starting a new age in the field of ion channels where study of structure-function relationships will take a central stage.

The earlier approaches used in modelling of ion channels such as reaction rate theories and continuum electrodiffusion equations are either not relevant or not appropriate for this purpose. The Brownian and molecular dynamics (BD and MD) simulation methods offer more promising approaches in this regard, and have been used in description of a number of ion channels recently (e.g. potassium, calcium and gramicidin). As in most biological processes, ion conductance through channels takes too long time (fraction of micro seconds) for a direct molecular simulation. Thus the coarse-grained BD method is required to determine conductance–the most important observable of an ion channel. Free energy calculations obtained from MD simulations provide complementary information to those of BD. For example, the selectivity of the potassium channels against the Na ions can be understood from MD studies but not from BD. In addition, the parameters employed in BD simulations, such as the diffusion coefficient of ions in a channel, can be determined from MD.

The force field parameters commonly used in MD simulations are mostly determined from fits to bulk properties, and their appropriateness for studying ion diffusion across channels is questionable (bulk water and protein channels provide very different environments for an ion). A direct evidence for this shortcoming is provided by the potential of mean force calculations in the gramicidin channel, which have invariably led to very large energy barriers that would have prevented ion conduction completely. The most important omission of the standard force fields

in this regard is the electronic polarizability of atoms. Development of polarizable force fields, either using phenomenology or ab initio MD methods is thus a priority area in current ion channel studies.

MEASUREMENTS OF THE CROSS-BRIDGE ATTACHMENT/DETACHMENT PROCESS WITHIN INTACT SARCOMERES BY THE SURFACE PLASMON RESONANCE

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The attachment of myosin to actin initiates the conversion of stored chemical energy to mechanical force production in smooth, skeletal, and cardiac muscles. We have developed a surface plasmon resonance (SPR) system to monitor the cross-bridge attachment/detachment process within intact sarcomeres from mouse heart muscle. SPR occurs when laser light energy is transferred to surface plasmons that are resonantly excited in a metal (gold) film. This resonance manifests itself as a minimum in the reflection of the incident laser light and occurs at a characteristic angle. The angle of the SPR occurrence depends on the dielectric permitivity of the sample medium adjacent to the gold film. Purified sarcomeric preparations are immobilized onto the gold film in the presence of a relaxing solution. Replacement of the relaxing solution with increasing Ca2+ concentration solution activates the cross-bridge interaction and produces an increase in the SPR angle. These results imply that the interaction of myosin heads with actin within an intact sarcomere changes the dielectric permmittivity of the sarcomeric structure. In addition, we further verify that SPR measurements can detect the changes in the population of the attached cross-bridges with altered concentrations of phosphate, 2.3 butanedione monoxime, or adenosine triphosphate at a fixed calcium concentration, which have been shown to reduce the force and increase the cross-bridge population in attached state. Thus, our data provide the first evidence that the SPR technique allows the monitoring of the cross-bridge attachment/detachment process within intact sarcomeres.

3D MESOSCOPIC CONTINUUM MODELS FOR ORGANELLES

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Current mathematical models for subcellular systems suffer from various serious drawbacks. On the one hand, the complex molecular intercellular interaction network leads to an explosion of parameters that are only partly accessible experimentally. On the other hand, each member of this network is localized in space: the system is built from very distinct compartments with shapes that adapt to the metabolism and external conditions. Most models simplify this spatial hierarchy by splitting purely reactive networks into separate containers. In theVCell project,

reaction-diffusion equations are solved in a static geometry obtained from experiments. In both cases, dynamic morphology changes are not captured. We propose an extension of our molecular field method, developed for the simulation of polymers, to incorporate and understand the basic mechanisms behind morphology formation and changes due to external and internal conditions. We will show first results for polymeric vesicles with fascinating internal structure.

COMPUTATIONAL DESIGN OF CALMODULIN DIRECTED TOWARDS IMPROVING ITS BINDING SPECIFICITY

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Although great progress has been achieved in predicting protein-ligand binding interactions, designing protein receptors from scratch remains a challenge. An intermediate step towards such design is to alter the binding properties of a natural receptor. Here we report the computational redesign of calmodulin (CaM), a small, ubiquitous Ca2+-binding protein that is known to bind to and regulate a variety of functionally and structurally diverse proteins. The CaM binding interface was optimized to improve binding specificity towards one of its natural targets, smooth muscle myosin light chain kinase ($smMLCK$). The optimization was performed using ORBIT (Optimization of Rotamers by Iterative Techniques), a protein design program that utilizes a physically based force-field and the Dead-End Elimination theorem to compute sequences that are optimal for a given protein scaffold. Starting from the structure of the $CaM - smMLCK$ complex, ORBIT searched through a library of amino acid side chain rotamers to obtain the lowest energy CaM sequence. Computationally designed CaM molecules were constructed and tested for binding to a set of six targets. The first optimization was performed on 24 core positions in the CaM binding interface. The calculation yielded an eight-fold mutant, CaM_8, that retained high binding affinity to the $smMLCK$ peptide (1.3 nM) and displayed reduced affinities to the other targets. Thus the binding specificity was increased 2 to 120-fold. The second calculation started from the CaM_8 sequence and optimized boundary and surface positions surrounding $smMLCK$. The resulting molecule, $CaM_1 4$, showed binding specificity similar to CaM_8, but displayed reduced affinity to $smMLCK$ (8.6 nM). The decrease in $CaM_1 4$s affinity to the main target was probably due to our inability to accurately model $CaM - smMLCK$ electrostatic interactions, which significantly enhance peptide binding. To solve this problem, the optimization procedure was modified to emphasize intermolecular interactions over intramolecular ones. The boundary and surface mutations predicted by this method resulted in a CaM variant with uncompromised affinity for $smMLCK$ and the highest binding specificity achieved so far.

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Peter Koenig, Theoretical Physics, University of Paderborn, PADERBORN, GERMANY

Hugo Kubyini, University of Heidelberg and BASF, LUDWIGSHAFEN, GERMANY

Serdar Kuyucak, Research School of Physical Sciences, Australian National University, CANBERRA, AUSTRALIA

Ilkka Lappalainen, Department of Biosciences, University of Helsinki, HELSINKI, FINLAND

Arthur Lesk, Wellcome MRC BUilding, University of Cambridge, CAMBRIDGE, UK

Jerzy Leszczynski, Department of Chemistry, Jackson State University, JACKSON, USA

Ming Liu, Centre for Molecular Simulation, Swinburne University of Technology, HAWTHORN, AUSTRALIA

Bengt Lundqvist, Department of Applied Physics, Chalmers University of Technology, GOTEBORG, SWEDEN

Alexander Lyubartsev, Department of Physical Chemistry, Stockholm University, STOCKHOLM, SWEDEN

Anthony Maggs, ESPCI, PARIS¡ FRANCE

Ricardo Luis Mancera, University of Cambridge, CAMBRIDGE, UK

Luca Maragliano, INFM and Department of Physics, University of Modena, MODENA, ITALY

Davide Marenduzzo, INFM-International School for Advanced Studies, TRIESTE, ITALY

Franci Merzel, National Institute of Chemistry, LJUBLJANA, SLOVENIA

Nuno Miguel Micaelo, Instituto de Tecnologia Quimica e Biologica, Universidade Nova de Lisboa, OEIRAS, PORTUGAL

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Joerg Neugebauer, Theory Department, Fritz Haber Institut der Max Planck Gesellschft, BERLIN, GERMANY

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Piotr Paneth, Institute of Applied Radiation Chemistry, Technical University of Lodz, LODZ, POLAND

Michele Parrinello, Swiss Center for Scientific Computing (CSCS/ETH), MANNO, SWITZERLAND

Marie Plazanet, Institut Laue Langevin, GRENOBLE, SWITZERLAND

Tonu Pulleritis, Chemical Physics, Lund University, LUND, SWEDEN

James Rabinowitz, National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, RESEARCH TRIANGLE PARK, USA

Charles Rhodes, Department of Physics, University of Illinois at Chicago, CHICAGO, USA

Ursula Rothilsberger, Laboratory of Inorganic Chemistry, ETH Zurich, ZURICH, SWITZERLAND

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Hans Schussler, Texas A&M University, COLLEGE STATION, USA

Klaus Schulten, Department of Physics, University of Illinois at Urbana-Champaign, URBANA, USA

Matthew Segall, Cavendish Laboratory University of Cambridge and ArQule Ltd, CAMBRIDGE, UK

Kaori Seino, Institut fur Festkorpertheorie und Theoretische Optik, Friederich Schiller Universitei Jena, JENA, GERMANY

Flavio Seno, INFM and Dipartimento di Fisica, Università di Padova, PADOVA, ITALY

Agur Sevink, Soft Condensed Matter Group, Gorlaeus Labs, Leiden Institute of Chemistry, LEIDEN, THE NETHERLANDS

Julia Shifman, Division of Biology, California Institute of Technology, PASADENA, USA

Per Siegbahn, Department of Physics, Stockholm University, STOCKHOLM, SWEDEN

Grigory Smolentsev, Faculty of Physics, Rostov State University, ROSTOV-NA-DONU, RUSSIA

Waclaw Sokalski, Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, WROCLAW, POLAND

Patricia Soto, Biophysical Chemistry, University of Groningen, GRONINGEN, SWEDEN

Francesco Spinozzi, INFM-Istituto di Scienza Fisiche, University of Ancona, ANCONA, ITALY

Dimas Suarez, Departamento de Quimica Fisica y Analitica, Universidad de Oviedo, OVIEDO, SPAIN

Noppowan Tanpipat, IBM, SAN DIEGO, USA

Anna Gabriella Tempesta, Department of Mathematics and Physics, KVL, FREDERIKSBERG, DENMARK

Alexander Louis Tournier, IWR Biocomputing Group, Universitat Heidelberg, HEIDELBERG, GERMANY

Antonio Trovato, Niels Bohr Institut, COPENAGHEN, DENMARK

Ilpo Tapio Vattulainen, Laboratory of Physics and Helsinki Institute of Physics, Helsinki University of Technology, ESPOO HUT, FINLAND

Bruno Lourenco Victor, Instituto de Tecnologia Quimica e Biologica, Universidade Nova de Lisboa, OEIRAS, PORTUGAL

Jordi Villa i Freixa, IMIM/UPF, Research Gropu on Biomedical Informatics, BARCELONA, SPAIN

Sinisa Vukovic, Department of Chemistry, University of Toronto, TORONTO, CANADA

Rebecca Wade, Molecular and Cellular Modeling, European Media Laboratory, HEIDELBERG, GERMANY

Arieh Warshel, Department of Chemistry, University of Southerm California, LOS ANGELES, USA

Rene Windiks, Condensed Matter Theory, Paul Scherrer Institut, VILLIGEN, SWITZERLAND

Haibo Yu, Physical Chemistry, ETH Zurich, ZURICH, SWITZERLAND

Wolfgang Zinth, BioMolekulare Optik, Sektion Physik, Ludwig-Maximilians Universitaet Muenchen, MUENCHEN, Germany

4.2.2 Report on EMRS Symposium A

SYMPOSIUM A- ATOMIC SCALE MATERIALS DESIGN
EMRS 2002 SPRING MEETING
STRASBOURG, FRANCE
June 18-21, 2002

Symposium A- "Atomic Scale Materials Design" of the European Material Research Society's Spring Meeting was held in Strasbourg, France during June 18-21, 2002 and was devoted to atomic scale computation applied to materials science problems. Although the areas of application for atomic scale computation are diverse, the underlying principles, algorithms and techniques are similar. Symposium A brought together researchers working on materials for electronics, materials growth, surface chemistry and catalysis, polymers, nanostructures, and intermetallics. The conference was generously supported by the Ψ_k network, the European Science Foundation, and the ATOMCAD network. The conference chairmen were:

Mehdi Djfari-Rouhani, CNRS-LAAS, Toulouse, France

Mike Finnis, The Queen's University Belfast, UK

Jim Greer, NMRC, Cork, Ireland

Jürgen Hafner, University of Vienna, Austria

Anatoli Korkin, Motorola Inc., Mesa, USA

The chairmen were assisted by the scientific committee comprised of:

G.Gilmer, Agere, USA

H.Goronki, Motorola, USA

M.Jaraiz, University of Valladolid, Spain

J.Labanowski, Ohio Supercomputer Center, USA

J.-L.Leray, Commissariat a l'Energie Atomique CEA/DAM, France

P.Lindan, University of Kent, UK

D.Pettifor, Oxford University, UK

M.Scheffler, Fritz Haber Institute, Germany

T.Vrotsos, Texas Instruments, USA

G.Wachutka, Technische Universitaet Muenchen, Germany

The following invited talks were presented:

LARGE SCALE SIMULATIONS WITH QUANTUM MECHANICAL FORCES, R.J. Bartlett, University of Florida, USA

ACCELERATED MOLECULAR DYNAMICS METHODS, A.F. Voter, Los Alamos, USA

MECHANICAL PROPERTIES AND THE CHEMICAL BOND, Ruben Perez, Universidad Autonoma de Madrid, Spain

MULTISCALE MODELING OF DEFECT KINETICS IN SEMICONDUCTORS, R.M. Nieminen, Helsinki University of Technology, Finland

SELF COMPENSATION IN FERROMAGNETIC SEMICONDUCTORS, S.C. Erwin, Naval Research Laboratory, USA

MAGNETISM OF MONATOMIC WIRES ON VICINAL SURFACES, D. Spisak, University of Vienna, Austria

AB INITIO MODELLING OF MOLECULAR ELECTRONIC DEVICES, K. Stokbro, Technical University, Denmark

CATALYTIC CONVERSION OF HYDROCARBONS IN ZEOLITES FROM FIRST PRINCIPLES, Lubomir Benco, University of Vienna, Austria

WHY IS A NOBLE METAL CATALYTICALLY ACTIVE? THE ROLE OF THE O-Ag INTERACTION IN THE FUNCTION OF SILVER AS AN OXIDATION CATALYST, C. Stampfl, Fritz-Haber-Institut, Germany

QUANTUM MONTE CARLO CALCUALTIONS OF HYDROGEN ADSORPTION ON Si(100), Claudia Filippi, University of Leiden, The Netherlands

GROWING CONTROLLED NANOCLUSTER FILMS, Pablo Jenson, Universite Claude Bernard, France

The symposium lasted four days covering the whole range of the 2002 E-MRS meeting. Over 100 contributions were selected with 40 oral presentations (11 of these invited) and the remainder were given as poster contributions. In order to cover the wide range of materials science disciplines, the contributions were scattered over the seven following sessions:

1. General session: covering new methods and algorithms recently developed to simulate the properties of materials
2. Semiconductor session: mainly devoted to the properties of bulk semiconductors and defect modelling
3. Spin Systems: bulk and thin film magnetic materials
4. Nanotechnology: discussions on molecular devices
5. Catalysis: fundamental mechanisms responsible for catalytic reactions
6. Biomolecules and Polymers: electronic and transport properties

7. CVD and Growth: focused the major issues in the development of future microelectronic devices

The presented papers will be published in the a special issue of the journal Computational Materials Science. Researchers from a total of 27 countries were present and participated to the symposium. We would like to thank the E-MRS for having accepted to host this symposium, the symposium sponsors Ψ_k, ESF, and ATOMCAD, and all of the participants who took the time and effort to make the EMRS Spring Meeting Symposium A a great success.

Abstracts of Oral Presentations in SYMPOSIUM A

Session I: General

A-I.1 LARGE SCALE SIMULATIONS WITH QUANTUM MECHANICAL FORCES
Rodney J. Bartlett, Carlos Taylor, Marshall Cory, Piotr Rozyczko and Keith Runge, Quantum Theory Project, University of Florida, Gainesville FL 32611, USA

Our goal is predictive simulations for materials. To achieve this, we introduce a simplified (transfer) Hamiltonian based upon coupled-cluster theory which can encode accurate quantum mechanical forces in a way that permits large scale MD to be performed in a multi-scale simulation, with up to approx. 1000 quantum mechancial atoms. We demonstrate different behavior under stress when using QM forces compared to classical ones for selected prototypes silica systems.

A-I.2 ACCELERATED MOLECULAR DYNAMICS METHODS
Arthur F. Voter, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

A significant problem in the atomistic simulation of materials is the time scale limitation of the molecular dynamics method. While molecular dynamics can easily access nanoseconds with empirical potentials, many of the most interesting diffusive events occur on time scales of microseconds and longer. If the transition state (i.e., the saddle point) for a given reaction pathway is known, transition state theory can be applied to compute a rate constant directly. If all possible events are known for a given system, these rate constants can be employed in a kinetic Monte Carlo algorithm to evolve the system from state to state over long time scales. Unfortunately, for realistic systems, the transition states are often hard to find. Moreover, it is often the case that our intuition about how the system will behave breaks down, so that key events are missing from the kinetic Monte Carlo treatment. This situation is typical in metallic surface growth, where complicated exchange events prevail, and in many other physically important processes, such as annealing after radiation damage, or diffusion at a grain boundary.

A-I.3 MECHANICAL PROPERTIES AND THE CHEMICAL BOND
Ruben Perez, Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma

de Madrid, Spain

The importance of a proper description, using quantum mechanics, of the atomic events that are ultimately responsible for the mechanical properties of materials is emphasized. Traditional approaches, based on classical potentials, failed to capture, in cases like brittle fracture, even the qualitative behaviour found in the experiments. However, it is nowadays possible to design and perform first-principles total energy calculations that reveal fundamental aspects of the microscopic origin of the observed macroscopic mechanical behaviour. These ideas are illustrated with applications to: Atomic Force Microscopy (AFM), where the simulations provide the basis for the interpretation of the atomic contrast observed in non-contact Frequency-Modulation AFM experiments, and the resolution limits in contact AFM.

A-I.4 COMBINED ELECTRONIC STRUCTURE AND EVOLUTIONARY SEARCH APPROACH TO MATERIALS DESIGN

Thomas Bligaard, Gisli Johannesson, Andrei Ruban, Hans Skriver, Karsten Jacobsen and Jens Norskov, Center of Atomic-scale Materials Physics, Departmant of Physics, Technical University of Denmark, Lyngby, Denmark

We describe the use of an evolutionary algorithm in conjunction with density functional theory to optimize material properties. The approach is illustrated by the search for the most stable four component alloys that can be constructed from 32 different metal elements in the periodic table. We immediately obtain well-known high-temperature super alloys like Ni3Al. The method also predicts that several other three and four component alloys should be equally stable and thus potentially interesting as high temperature alloys.

A-I.5 ARE DFT LEVEL CALCULATIONS THE ANSWER TO REAL-WORLD MOLECULAR SYSTEMS?

Robert J. Meier, DSM Research, P.O.Box 18, 6160 MD Geleen, The Netherlands

This contribution is intended to initiate discussion on the performance of first principles calculations for molecular systems. Since quantum mechanics was formulated, we have seen significant development in both theory as well as application. Lack of computing power has long limited application to many practical, real-world, systems. Compared to a decade ago, however, it is now possible to study molecular species of a size that is becoming relevant for both the academic as well as for the industrial chemist. But how good are the numbers we generate using such, nowadays almost exclusively, DFT calculations? Whereas hybrid methods such as B3LYP often show good compromise between accuracy and computational cost compared to, e.g., MP2, in some important cases the DFT approach does not yield appropriate results, sometimes even leading to unreliable answers. In this talk this will be illustrated. We will discriminate between what we will call accuracy and reliability. In addition, throughput of calculations is a real bottleneck. What we need are quantum computational methods providing us with reliable (relative) energies, for systems up to say a hundred atoms. Such calculations should be possible

on a routine basis. We plead for a set of benchmark systems to evaluate newly introduced functionals, and mutually compare performance of existing methods.

Session II: Semiconductors

A-II.1 MULTISCALE MODELING OF DEFECT KINETICS IN SEMICONDUCTORS

R.M. Nieminen, COMP/Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland

The interplay between non-equilibrium defects, impurities and dopants is crucial for the behavior of semiconductor structures upon processing and annealing. We combine atomistic calculations for the energetics and structures of defect complexes with rate equation, kinetic Monte Carlo, and cellular automaton simulations of long time and length scale phenomena. As specific applications, we discuss oxygen clustering in silicon, anisotropic chemical etching of silicon surfaces, and self-diffusion in gallium antimonide.

A-II.2 SUBSTITUTIONAL N-TYPE DOPING OF DIAMOND

Karin Larsson, Department of Materials Chemistry, Angstrom Laboratory, University of Uppsala, Uppsala, Sweden

One of the major topics in diamond science and technology today is the search for a suitable donor impurity in diamond which can be introduced into the diamond lattice and which has a donor level close enough to the conduction band minimum. A substitutional n-type doping of diamond during CVD growth has been studied in the present investigation. This incorporation mode depends on both the kinetics of the growth process and the solubility of the impurity. Kinetic trapping may then be possible although the final n-type doped product is thermodynamically very unfavourable. Calculations have in the present study been carried out for N, P and S impurities using the DFT and Hartree-Fock levels of theory. The effect of i)chemisorption of hydrogenated impurity species and the following substitutional incorporation into the ii) upper surface atomic layer and iii) bulk position, on materials properties like thermodynamics, solubilities, geometrical structures and electronic structures, have been of a special interest to study more thoroughly. The results in the present investigation clearly show that the trend in diamond (111) surface reactivity towards N(or P or S)-containing gaseous species, does generally not follow the corresponding trend in solubility. However, the N impurity have the largest solubility and the surface shows the most pronounced surface reactivity towards the NHx species (X=0-3).

A-II.3 THERMAL TRANSPORT ACROSS SiC/METAL INTERFACES AND CONTACTS

Eleni Ziambaras and Per Hyldgaard, Department of Applied Physics, Chalmers University of Technology and Goteborg University, 41296 Goteborg, Sweden

The SiC/metal contacts and interfaces are heterostructured materials and can inhibit thermal

transport even though both SiC and metals are excellent thermal conductors. The semiconducting nature of SiC limits the interface thermal transport to phonons. Such phonon transport can suffer both dramatic scattering and total-internal reflection effects[Phys. Rev. B 56, 10754 (1997)]. The intended use of SiC for high-power semiconducting devices motivates a larger investigation of consequences for the thermal stability of SiC contacts — can we make robust soldering? Here we present calculations of both the SiC/Al-interface structure and thermal transport. We model the interface atomic relaxation and dynamics and use a Boltzmann-equation approach to study the phonon transport. We document important thermal-conductivity reductions arising from the significant difference in material hardness (total-internal reflection effects) at the SiC/Al interface and we initiate the study of phonon scattering and transport in SiC/metal contacts

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A-II.4 FIRST PRINCIPLES DETERMINATION OF HIGH EFFICIENCY NEW PHOTOVOLTAIC MATERIALS

P. Wahnon, P. Palacios and C. Tablero, ETSI Telecomunicacion, Universidad Politecnica de Madrid, 28040 Madrid, Spain

The aim of this work is to investigate within a DFT quantum mechanical framework the possibilities of a new material, with improved optoelectronic properties, in order to produce a new photovoltaic device with a significant increment of the theoretical limiting efficiency of conventional solar cells. To reach that, we study at atomic level, the characteristics of a new photovoltaic semiconductor material with an isolated metallic intermediate band located in the semiconductor energy band gap. Our final purpose is to determine the potential for photovoltaic conversion of this structure by establishing its limiting efficiency. In a previous work, using an accurate First Principles method we proposed an alloy semiconductor containing Ti atoms, of the type: TiGamXn with X=As or P, that presents an isolated half filled intermediate band. Our purpose here is, to present this kind of band diagram characteristics and phonon dispersion studies for several alloys compounds. For this work, we use the ab-initio Siesta code based on density functional techniques. In such a method the exchange and correlation energy is calculated in the LDA and GGA approximations. The Siesta code builds up the force constant matrix needed to determine the phonon dispersion diagram. A preliminary limiting efficiency of 46these compounds using a procedure of calculation developed in a previous work.

Session III: Spin Systems

A-III.1 SELF-COMPENSATION IN FERROMAGNETC SEMICONDUCTORS

Steven C. Erwin, Center for Computational Materials Science, Naval Research Laboratory, Washington DC, USA

Ferromagnetism in Mn-doped GaAs is generally believed to be mediated by holes arising from substitutional Mn. Measured hole concentrations are much smaller than expected from simple electron counting, for unknown reasons. We present theoretical evidence that the source of this

compensation is interstitial Mn. We show that under non-equilibrium conditions characteristic of the low temperatures used during growth, interstitial Mn can be formed by a simple low-energy surface adsorption process. In the bulk, interstitial Mn plays a dual role: as a source of hole compensation, and as a source of localized spins whose interactions are mediated by electrons. We develop a mean- field theory of magnetism that self-consistently accounts for both substitutional and interstitial Mn as well as their mutual compensation.

A-III.2 ELECTRONIC PROPERTIES OF Mn-COMPOUNDS UNDER STRAIN

A. Debernardi, M. Peressi and A. Baldereschi, Instituto Nazionale per la Fisica della Materia (INFM), Trieste, Italy

The recent discovery of giant magneto-resistance has driven increasing interest to the study of magnetic materials. The main target is the design and the realization of new devices with materials whose magnetic properties could be tailored in accordance to the needs of electronic industry. Within the solid state community is rapidly becoming popular the word "spintronic" to denote electronic-like heterostructures where the relevant physical quantity is the spin of the carriers and its interactions with external magnetic fields rather than the charge of holes and electrons and the associated electronic properties. In this context the most promising materials are Mn compounds, grown on different semiconductor substrates. A recent experiment has proved the possibility to grow ordered films (heterostructures) of MnAs on ZnSe. The presence of a ZnSe buffer layer exclusively stabilizes a particular phase ("type-B") of MnAs; at variance, the coexistence of different phases in the magnetic epitaxial layers is experimentally observed when the substrate is GaAs. Due to lattice mismatch the Mn-compound epilayer display a deformed structure with respect to the bulk one, i.e. the structure is strained. We present first-principles calculation of electronic structure of Mn-based compounds under strain. Our calculation is done within the framework of density functional theory by using the plane wave pseudopotential method.

A-III.3 FIRST PRINCIPLE STUDY OF ELECTRONIC STRUCTURE AND TOPOGRAPHY OF ADSORBED METALLIC QUANTUM DOTS

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V. Lindberg, Dept. of Physics, School of Mathematics and Systems Engineering, Vxj University, 35252 Vxj, Sweden,
M.J. Puska, Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland
B. Hellsing, Dept. of Physics, Chalmers University of Technology, 412 96 Goteborg, Sweden

We have modeled a one monolayer (ML) thick Na quantum dot (QD) on a Na covered Cu(111) surface, with focus on the electronic structure and real space topography. The surface electron states are obtained by substituting the Na layer by jellium with parameters close to those used for bulk Na metal. The influence of the Cu(111) substrate is taken into account by introducing a

layer of less dense jellium below the Na layer. The QD's are assumed to be cylindrical in shape. The calculations are based on the Density functional theory applying the MIKA (Multigrid Instead of the K-spAce) real-space multigrid method. To fit the parameters we have studied a free standing Na ML and 1 and 2 ML Na on Cu(111), and compared with theoretical and experimental results. As a reference we have also studied a 1 and 2 ML thick free standing cylindrical QD. The system of a one ML Na QD adsorbed on a substrate formed by one complete Na ML on Cu(111) is carefully studied. The MIKA package provides us with the possibility to perform calculations on large systems with thousands of electrons and to accurately calculate the wavefunctions in regions of low valence electron density. The local density of states (LDOS) are calculated and compared with differential conductance (dI/dV) spectra and constant current topographs from Scanning Tunneling Microscopy.

Session IV: Nano Technology

A-IV.1 MAGNETISM OF MONOATOMIC WIRES ON VICINAL SURFACES

D. Spisak, Institut für Materialphysik, Universität Wien, Sensengasse 8/12, 1090 Wien, Austria

There are three key steps in the development of one-dimensional nanostructures: fabrication, characterization and application. In our contri-bution we concentrate on the second step, characterization of the structure and magnetic behaviour of monoatomic wires grown on Cu and Ag surfa-ces with a high density of steps from the theoretical point of view. At first, the geometry of clean Cu(11n) and Cu(10n) vicinal surfaces is optimized by means of calculated interatomic forces, and the formation energies of steps along the 110 and 100 direction are compared with experimental estimates. In the following, the monoatomic Fe wires are placed at various positions onto Cu substrate. The preferential positions of wires are predicted to be the inner corner sites of the steps. From the total energy differences between ferromagnetic and antiferromagnetic configu-rations the effective intrawire and interwire magnetic coupling constants are estimated. In all investigated cases the resulting magnetic order is ferromagnetic. Regarding an array of wires as a quasi-2D XY ferromagnet we find the Curie temperature of the system using Monte Carlo simulation. Finally, a possibility of magnetism in monoatomic wires made of 5th and 6th row elements, which are nonmagnetic in bulky structure, is explored and discussed. The obtained results are in complete agreement with the known trends that a reduced dimensionality promotes magnetism.

A-IV.2 AB INITIO MODELLING OF MOLECULAR ELECTRONICS DEVICES

Mads Brandbyge(a), Jeremy Taylor(a), Jose-Luis Mozos(b), Pablo Ordejon(b) and Kurt Stokbro(a), (a)Mikroelektronik Centret, Technical University of Denmark, 2800 Lyngby, Denmark, (b)Institut de Ciencia de Materials de Barcelona, CSIC Campus de la U.A.B., Spain

I will present our newly developed method, TranSIESTA[1,2], which enables a full atomistic description of nanosized electronics devices under operation conditions. The method is based on

density functional theory, and uses local basis sets[3] combined with a non-equilibrium Greens function transport scheme. With this package it is possible to calculate the selfconsistent electronic structure, electrical current, and current induced forces of a nanostructure coupled to 3-dimensional electrodes with different electrochemical potentials, using a full atomistic ab initio description of the entire electrode and the nanostructure. One of the most popular methods to couple molecular devices to external electrodes is via thiolate bonds. One of the key characteristics of such a device is the corresponding contact resistance, however, different experiments seem to give conflicting results for the inherent resistance of a thiol bond. I will present theoretical results for the IV characteristics of different organic molecules coupled to gold electrodes via thiolate bonds and compare with the corresponding experimental data. In several experiments the molecules have an asymmetric coupling to the external electrodes and I will show how this asymmetry may lead to rectification in the device.

A-IV.3 AN ACCURATE THEORETICAL APPROACH FOR ELECTRON TRANSPORTATION PROPERTIES of SINGLE MOLECULAR DEVICES

Yi Luo, Theoretical Chemistry, Department of Biotechnology, Royal Institute of Technology, SCFAB, 10691 Stockholm, Sweden

We have developed a new theoretical approach to characterize the electron transportation process in molecular devices based on the elastic-scattering Green's function theory in connection with the hybrid density functional theory without using any fitting parameters. Two molecular devices with benzene-1,4-dithiol and octanedithiol molecules embedded between two gold electrodes have been studied. The calculated current-voltage characteristics are in very good agreement with existing experimental results reported by Reed et. Al for benzene-1,4-dithiol [Science, 278(1997) 252] and by Cui et al. for octanedithiol [Science, 294(2001) 571]. Our approach is very straightforward and can apply to quite large systems. Most importantly, it provides a reliable way to design and optimize molecular devices theoretically, thereby avoiding extremely difficult, time consuming laboratory tests.

Session V: Catalysis

A-V.1 CATALYTIC CONVERSION OF HYDROCARBONS IN ZEOLITES FROM FIRST PRINCIPLES

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(b)Totalfinaelf, Centre Europeen de Recherche et Technique, Harfleur, France

Conversion of hydrocarbons over zeolites is important industrial process used in the production of petrol. The microscopic steps of the conversion, however, are still not fully understood. In order to examine reaction pathways we have performed static and molecular dynamics DFT calculations on gmelinite zeolite and linear saturated and unsaturated hydrocarbon molecules. The conversion can proceed through the through the chemisorption of olefins at the inner surface

of the zeolite. The desorption of chemisorbed species produces unstable protonated molecules. The protonated hydrocarbons are long-lived being stabilized in the zeolite surroundings. They are considerably deformed and at increased temperatures (700K) high mobility of the H atoms along the molecular chain is observed. The relocation of the H atom can lead to the formation of structures with maximum stabilization of the positive charge, such as molecules with tertiary C atoms and cyclo-structures of hydrocarbons. The back donation of the proton to the zeolite framework can cause collapse of the linear protonated molecule, as well. Both cracked and isomerized products can be formed upon the back donation. Depending on the O...H-C contact established between the molecule and the framework the H atoms are removed from different C atoms thus starting either cracking or isomerization of the hydrocarbon molecule.

A-V.2 DYNAMICS OF HYDROGEN MOLECULES ON METAL ALLOY SUFACES-PROBING LOCAL SURFACE REACTIVITY WITH HYDROGEN

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(d)Departamento de Fisica de la Materia Condensada C-III, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain,
(e)Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

The hydrogen on metal surfaces system has, through the past years, become a paradigm for studying dynamical quantum processes on solid surfaces. Previously, we presented reports on the dynamics of H2 on single component metal surfaces, focusing on the orientational dependence of hydrogen-metal surface reactions. We then extended our study to consider the dissociative adsorption dynamics of H2 interacting with a metal alloy (esp., binary component) surface, viz., Cu3Pt(111). Here, we compare the dynamics of H2 reaction with two binary component metal surfaces, viz., Cu3Pt(111) and NiAl(110). We will show how scattering dynamics studies, complementing dissociative adsorption studies, could give us a microscopic picture of why H2 dissociation on Cu3Pt(111) is globally non- activated, and activated on NiAl(111). We will discuss the dynamics of H2-solid surface interaction in the context of the feasibility of utilizing H2 as a unique experimental tool to directly probe the adsorbate-surface interaction potential, etc. (KEYWORDS: hydrogen, deuterium, metal alloy, scattering dynamics, potential energy surface, dynamics calculation, ab initio quantum dynamics calculations, Cu(111), Pd(111), Cu3Pt(111), NiAl(110)).

A-V.3 COMPUTER SIMULATION OF SPUTTERING AND OXYGEN DESORPTION PROCESSES AT GRAZING ION BOMBARDMENT OF Ag(110) SURFACE

A.A. Dzhurakhalov, S.E. Rahmatov, N.A. Teshabaeva, Arifov Institute of Electronics, F.Khodjaev Str.33, 700187 Tashkent, Uzbekistan

The sputtering and desorption processes give the information about crystal structure and property of materials and vacuum devices. In the present work the ion sputtering and oxygen desorption processes at 5 keV Ne ion bombardment of clean and oxygen covered Ag(110) surface have been investigated by computer simulation. The trajectories of the colliding particles were constructed as a sequence of binary collisions. The particle interactions were described by the universal Biersack-Ziegler-Littmark potential. The inelastic energy losses have been calculated by modified Firsov model and included into the scattering kinematics. The presence of a planar energy barrier on the surface was taken into account. The energy and angular distributions of particles sputtered and desorbed from the surface, as well as their yields have been calculated as a function of polar and azimuth angle of incidence. The dissociative and non-dissociative desorption yields of oxygen admolecules have been studied in detail. In the angular distributions of desorbed particles the maxima corresponding to the preferential ejection directions have been observed. It was established that in the case of grazing ion bombardment the probability of non-dissociative desorption of diatomic molecules is large and depends strongly on crystal orientation. Application of calculated results to study the sputtering and desorption processes on the single crystal surface under grazing ion bombardment is discussed.

A-V.4 WHY IS A NOBLE METAL CATALYTICALLY ACTIVE? THE ROLE OF THE O-AG INTERACTION IN THE FUNCTION OF SILVER AS AN OXIDATION CATALYST

Catherine Stampfl, Weixue Li, Matthias Scheffler, Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin-Dahlem, Germany

Silver is an important industrial catalyst for the epoxidation of ethylene to epoxide and the partial oxidation of methanol to formaldehyde; two of the most versatile chemical intermediates. Despite huge research efforts, due to the pressure and materials gap separating the real world of catalysis from the ideal world of well-characterized standard Surface Science experiments, there is an acute lack of understanding of the function of silver as an oxidation catalyst on the microscopic level. Extensive density-functional theory calculations, and taking into account temperature and pressure, provide a comprehensive picture of the behavior and interaction of oxygen and silver, and help explain why silver, as a noble metal which binds adparticles only weakly, is a remarkably efficient catalyst. Among other things we find that low coverages of oxygen chemisorbs on Ag(111), but for coverages greater than $\sim$0.25 ML sub-surface sites are occupied and surface-oxide like structures form. Sub-surface oxygen as well as defects significantly strengthen the surface oxygen- metal bond, allowing oxygen to stay on the surface and to participate in reactions. At the very high temperatures ($\sim$900 K) of certain oxidizing reactions, however, only oxygen species adsorbed at pre-existing surface defects are thermodynamically stable.

A-V.5 THE 3SQRT(3)x3SQRT(3) RECONSTRUCTION OF ALUMINA(0001)

Thierry Deutsch, CEA-Grenoble DRFMC/SP2M
Frederic Lanron, CEA-Grenoble DRFMC/SP2M, France,
Igor Vilfan, Inst. J. Stefan, Ljubljana, Slovenia

We present a new method of obtaining the real-space structure of complex surface reconstructions from incomplete scattering data. Usually, the experiments provide us only the non-integer-order diffraction intensities and, after Fourier transform, an incomplete Patterson map. Computer simulations based on the energy minimisation are implemented to obtain the missing intensities of the integer-order peaks and the structural information from such a map. The method is used to analyse the atomic structure of the Al-rich $(3\sqrt{3} \times 3\sqrt{3})\mathrm{R}30^\circ$ reconstructed surface of sapphire $\alpha{-}\mathrm{Al_2O_3}(0001)$. In the simulations, the interactions between the Al overlayer atoms were described with the Sutton-Chen potential and the interactions between the overlayer and the sapphire substrate with a laterally modulated Lennard-Jones potential. We have shown that the hexagonal reconstructed unit cell is composed of triangles where the two layers of Al adatoms are FCC(111) ordered whereas between the triangles the stacking is FCC(001).

A-V.6 ATOMISTIC VIEW OF THE HETEROEPITAXY ON AN INHOMOGENEOUS SUBSTRATE

Christine Goyhenex, Herve Bulou, Carlo Massobrio, CNRS, IPCMS, 23 rue du Loess, 67037 Strasbrg Cedex, France

The ability to incorporate nanostructures in fields like microelectronics or magnetic recording is a challenge for the developments towards high density storage and large-scale integration. The main difficulty is to produce large quantities of nanostructures in a controlled manner. The herringbone surface reconstruction of Au(111) offers an efficient way to grow collections of clusters homogeneous both in size and density. Many experiments have been carried out on systems where X species (X=Fe,Co,Ni,Cu,Rh) nucleate at the kinks sites of the Au(111) reconstruction leading to regular arrays of clusters. However the understanding at the atomic scale of the organization of these systems is far from being complete. This is mostly due to the complex morphology of the substrate giving rise to a wide distribution of bond distances when atoms are deposited on it. In this contribution, we present a study of the system Co/Au(111) in the framework of atomistic tight-binding molecular dynamics simulations. The inhomogeneous strain state of the gold reconstructed surface is expected to play an important role in the microscopic mechanisms of the growth. Therefore we focus on the local hydrostatic stress maps to characterize the stress distribution and its modifications upon adsorption and incorporation of Co atoms in the surface. First results on the effect of the inhomogeneity of the substrate on atomic diffusion will be also shown.

Session VI: Bio Molecules and Polymers

A-VI.1 FREE ENERGY SIMULATIONS COME OF AGE: PROTEIN—LIGAND RECOGNITION

Thomas Simonson, CNRS, Strasbourg, France, Georgios Archontis, U.of Cyprus, and Martin Karplus, U. of Strasbourg and Harvard University, USA

In recent years, molecular dynamics simulations of biomolecular free energy differences have ben-

efited from significant methodological advances and increased computer power. Applications to molecular recognition provide an understanding of the interactions involved that goes beyond, and is an important complement to, experimental studies. Poisson-Boltzmann electrostatic models provide a faster and simpler free energy method in cases where electrostatic interactions are important. We illustrate both molecular dynamics and Poisson-Boltzmann methods with a detailed study of aminoacid recognition by aspartyl-tRNA synthetase, whose specificity is important for maintaining the integrity of the genetic code.

A-VI.2 AB INITIO TIGHT-BINDING STUDY OF EXCITON OPTICAL AND ELECTRO-OPTIC PROPERTIES OF CONJUGATED POLYMERS

Thomas G. Pedersen and Thomas B. Lynge, Institute of Physics, Aalborg University, Pontoppidanstraede 103, 9220 Aalborg East, Denmark

Recovery of implantation defects is of paramount importance for applications of SiC in semiconductor devices. Up on implantation heavy ions produce along their tracks amorphous zones, which when overlapping at high fluences (¿1014 cm-2) form a continuous amorphous band. Crystallization of this band requires temperatures higher than 8000C, while crystallized material might consist of many polytypes of SiC with different properties, hampering economic production. It is known that crystalline SiC can be prevented from turning amorphous by choosing implantation temperatures above 6000C. Therefore, it is likely that single cascade damage will recover at about this temperature. In order to perform a detailed study on the recovery of amorphous zones created by individual ions, defects created by very low fluences of Xe ions have been monitored by PBA. Positrons are very sensitive to defects, so that at fluences as low as 4108 420 keV Xe cm-2 positron trapping has been observed. The fraction of positrons trapped in defects corresponds to results of a model where diffusion limited trapping was assumed in disordered zones predicted on the basis of SRIM calculations. The fraction increased linearly with fluence and saturation effects appeared at fluences ¿51012 cm-2. Similar implantations in Si and diamond, which are no compound materials, induced much less damage. Thermal recovery and recovery kinetics of the amorphized zones in 6H- SiC and in epitaxial 3C-SiC on Si are discussed.

A-VI.3 PPV AND PDA INTRA-MOLECULAR CHARGE MOBILITY SIMULATED BY QUANTUM MOLECULAR DYNAMICS

A.M. Almeida, Marta M.D. Ramos and Helena G. Correia, Departamento de Fisica, Universidade do Minho, Largo do Pato, 4700-320 Braga, Portugal

The growing interest in organic semiconductor based devices together with the most recent computational facilities has allowed the extensive use of simulations to study large molecular systems anticipating some of their individual physical properties. The simulation of a device such as a light emitting diode (LED), whose active media is a polymeric material, demands a well-founded knowledge of how a molecule behaves under specific conditions, namely how an injected charge accommodates in a molecule and the way it drifts under the action of an external electric field. The results presented here refer to two wide used polymers (poly(p-phenylene-vinylene) (PPV)

and poly-diacetylene (PDA)) showing how small and medium size molecules, either with a single net charge or containing an exciton, respond to an external electric field. In our calculations we have used a self-consistent quantum molecular dynamics method, which has the ability for simulating the transport of the injected charge along each molecule, thus providing an estimate of the charge mobility. Our results suggest there are two charge conduction regimes. The minimum value of the electric field strength to cause charge displacement was also predicted. Differences have been found in the charge mobility depending on the polymer chemistry. The effect of stretching of the PPV molecule has also been studied.

A-VI.4 APPLYING PERIODIC DENSITY FUNCTIONAL THEORY METHODS FOR SOLID STATE CHEMICAL PHYSICS ? MODELLING INTER AND INTRA-MOLECULAR INTERACTIONS IN BIOLOGICALLY RELEVANT HYDROGEN-BONDED NETWORKS

Mark Johnson, Insititut Laue Langevin, Grenoble, France

The extension of quantum chemistry methods from small isolated molecules to periodic solids containing up to 1000 atoms has allowed the focus of computational work in chemical physics to shift from intra-to inter-molecular interactions. The quantum tunnelling of molecular rotors is a simple, extremely sensitive probe of inter-molecular interactions and has been used to evaluate solid state density functional theory (DFT) methods in this context. Molecular vibrations constitute an intrinsically more complex, multi-dimensional problem, but the same DFT methods generally allow vibrational spectral profiles, measured by inelastic neutron scattering, to be accurately reproduced. In particular solid state methods are particularly well suited to modelling vibrational modes in hydrogen-bonded systems in which the inclusion of such strong inter-molecular interactions can shift the single molecule frequencies by a factor of two. Calculations on model hydrogen-bond compounds will be shown; hydrogen-bonded dimers, one-dimensional hydrogen-bonded molecular chains, bases and nulceosides in higher dimensional hydrogen-bonded networks. Perspectives for moving, experimentally and computationally, on to real hydrogen-bonded systems, like DNA and polypeptides, will be discussed.

Session VII: CVD and Growth

A-VII.1 QUANTUM MONTE CARLO CALCULATIONS OF HYDROGEN ADSORPTION ON Si(100)

Claudia Filippi, Instituut-Lorentz, Universiteit Leiden, The Netherlands

The Si(100) surface has become a paradigmatic system to test our general understanding of surface physics and chemistry. Despite extensive experimental and theoretical investigation, fundamental aspects of the interaction of molecular hydrogen with the Si(100) surface are still subject to debate. We revisit the topic using large model clusters of the surface and quantum Monte Carlo techniques to accurately account for electronic correlations. Our calculations predict reaction energies and barriers significantly higher than approximate density functional theory calculations. The higher adsorption barriers are in better agreement than previous DFT

results with the observed low sticking coefficient of H2 on Si(100). Various adsorption/desorption mechanisms will be discussed.

A-VII.2 FROM SILICON OXIDE TO HIGH-K DIELECTRICS: A CHALLENGE FOR COMPUTATIONAL MATERIAL SCIENTISTS

Gennadi Bersuker and Howard R. Huff, International SEMATECH, 2607 Montopolis Dr., Austin, TX 78741, USA

Aggressive device scaling calls for gate dielectrics with smaller effective oxide thickness, down to 1 nm and even 0.5 nm, and raises concerns about their reliability. Extensive research efforts to identify the key factor controlling electrical properties of SiO2 films have not yet yielded a comprehensive model, while our understanding of the high-k materials is even further away. Modeling efforts, which target experimentally well-defined issues, are essential for speedy progress. Ab initio calculations of the bulk and interfacial layer of SiO2 have identified the localized states in the oxide band gap associated with oxygen-related defects. Electron capture by these states were shown to lead to Si-O bond breakage and eventually the generation of paramagnetic E'centers. This scenario for oxide degradation phenomenon in the direct tunneling regime found support in accelerated electrical stress measurements. Leakage currents in high-k films (ZrO2, HfO2, and their silicates) were also attributed to electrically active localized states; these states were calculated to be induced by metal ions in conjunction with oxygen vacancies and oxygen interstitials. However, the range of experimental effects of great practical importance are yet largely un-addressed and ripe for modeling explorations.

A-VII.3 STUDY OF SILICON NANO-CLUSTER SELF-LIMITING OXIDATION BY ATOMISTIC SIMULATIONS

J. Dalla Torre, J.-L. Bocquet, Y. Limoge, J.-P. Crocombette, E. Adam, G. Martin, CEA Saclay, SRMP, Gif-sur-Yvette, France,
T. Baron, LTM, Grenoble, France,
P. Rivallin, P. Mur, CEA Leti, SRD, Grenoble, France

Oxidation of silicon nano-spheres or -cylinders is known to develop stresses that yield a self-limiting oxidation behavior which is of practical interest. It may be used to control the size and the size distribution of a cluster assembly, of importance e.g. in quantum dots based single electron devices. Stress is expected to affect the oxide formation energy, the oxidant diffusion or reaction at the silicon/oxide interface. We study the silicon oxidation by molecular dynamics simulations using an extended Stillinger- Weber interatomic potential for Si, O mixed systems developed by Watanabe and co-workers. Oxygen atoms are directly inserted in the Si-Si bonds to form the silicon oxide. Using this technique, we can compute the local stress in the system as the oxide grows. We tested first the model on the oxidation of flat Si substrates. Next, the oxidation of spherical clusters is presented. We show that continuum models fail to give the correct evolution of stresses as a function of the oxide shell thickness and that pressure variations through the oxide shell can have large effects on the oxidant transport to the Si nucleus.

A-VII.4 GROWING CONTROLLED NANOCLUSTER FILMS Pablo Jensen, Departement de Physique des Materiaux, UMR CNRS 5586, Universit Claude Bernard Lyon-1, 69622 Villeurbanne Cedex, France

I will present recent results on the growth of nanostructured films prepared by cluster deposition. After the surprisingly high values for cluster diffusivity found on graphite surfaces, we investigated cluster diffusion on a variety of different substrates, to understand technologically important experimental issues. The simulation results are compared to experiments.

A-VII.5 AB INITIO MODELLING OF OXYGEN DEFECTS IN GATE OXIDES A.S. Foster, V.B. Sulimov, P.V. Sushko, F. Lopez Gejo, A.L. Shluger and R. Nieminen, Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 Helsinki, Finland and Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK

Modelling of point defects induced by growth and subsequent annealing of oxide films is important for their applications as gate oxides. Using periodic plane wave DFT and embedded cluster methods we have studied the structure and electronic properties of neutral and charged oxygen defects in three prototype gate oxides: monoclinic ZrO2 and HfO2, and amorphous SiO2. The structure, ionisation energies and electron affinities of oxygen vacancies and interstitial oxygen atoms and molecules in different charge states were calculated. The positions of defect levels with respect to the bottom of silicon conduction band are determined. The results demonstrate that interstitial oxygen atoms and molecules, and positively charged oxygen vacancies can trap electrons from silicon. Diffusion mechanisms of oxygen species and vacancies are analysed and their role in degradation of gate oxides is discussed.

A-VII.6 HETEROEPITAXIAL GROWTH OF HIGH-K GATE OXIDES ON SILICON: INSIGHTS FROM FIRST-PRINCIPLES CALCULATIONS
Clemens J. Först(a,b), Peter E. Blöchl(a) and Karlheinz Schwarz(b), (a)Institute for Theoretical Physics, Clausthal University of Technology, Leibnitzstra?e 10, 38678 Clausthal-Zellerfeld, Germany,
(b)Institute for Material Chemistry; Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria

Scaling of semiconductor devices currently results in structures with nearly atomic dimensions. Gate oxides, which separate the switching current from the drive current in a MOSFET transistor, are approaching a thickness range of only few atomic layers, so that quantum-mechanical leakage currents become intolerable. New insulating materials with larger dielectric constants, e.g. high-k oxides, can be implemented at a larger physical thickness with electrical properties equivalent to those of an ultrathin conventional gate oxide. We present the results from ab-initio molecular dynamics simulations using the projector augmented wave method on the heteroepitaxial growth of high-k oxides on silicon.

A-VII.7 THEORY OF THE PHASES AND ATOMISTIC STRUCTURE OF YTTRIA-DOPED ZIRCONIA

S. Ostanin, E. Salamatov, A. Craven, D. McComb, A. Alavi, A.T. Paxton, M. Finnis, Department of Physics, University of Warwick, Coventry CV4 7AL, UK, Physico-Technical Institute, Ural Branch of RAS, Izhevsk 426001, Russia,
Department of Physics, University of Glasgow, Glasgow G12 8QQ, UK,
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK,
Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK,
School of Mathematics and Physics, Queen's University, Belfast BT7 1NN, UK

The electronic structure of yttria-stabilised zirconia for compositions between 3 and 15 mol has been computed using a pseudopotential based technique to calculate the local relaxations near the O vacancies. The phase transition from the tetragonal to cubic phase predicted at 10 mol reproduces experimental observation. Using the relaxed defect geometry, calculation of the electron energy-loss near-edge structure (ELNES) was carried out using the full-potential linear muffin-tin orbital method. The results show very good agreement with the experimental O K-edge signal, demonstrating the power of using ELNES to probe the stabilization mechanism in doped metal oxides. In the displacive limit of the double-well potential model, the vibration mode corresponding to the soft phonon in pure cubic zirconia has been calculated for each composition of yttria. These anharmonic vibrations were investigated within the self-consistent phonon approximation making obtanable the fine structure in spectral density. The displacement probability density calculated can quantify very accurately the transition temperature necessary for stabilizing the cubic phase.

A-VII.8 TRANSPORT LIMITATION EFFECTS OF ATOMIC LAYER DEPOSITION IN HIGH ASPECT RATIO STRUCTURES

A. Kersch, G. Schulze-Icking, Infineon Technologies AG, Memory Products, Balanstrasse 73, 81541 Munich, Germany

One possible cause for non-ideal ALD growth are insufficient cycle times which can result in an unsaturated surface coverage, at least at some positions of a microscopic structure. We have developed a Monte-Carlo transport simulation technique coupled to a feature scale simulator to investigate the time evolution of surface coverages during the ALD deposition step. For different precursor sticking coefficients and for structures with different aspect ratios we have calculated the minimal time required to reach complete surface saturation. Furthermore we have calculated the front of the grown film after several cycles. Our results clearly indicate that for extreme aspect ratios the cycle frequency may be limited by the gas transport inside the feature. This effect has so far been neglected but needs to be taken into account for future ALD process and equipment developments for DT processes.

A-VII.9 AB INITIO INVESTIGATION OF BASIC MECHANISMS DURING HfO2 DEPOSI-

TION ON Si

Leonard Jeloaica, Alain Esteve, Daniel Esteve, LAAS-CNRS, 7 av. du Colonel Roche, 31077 Toulouse, France,
Mehdi Djafari Rouhani, Laboratoire de Physique des Solides, 118 route de Narbonne, 31062 Toulouse, France

Use of high-k dielectric materials has been suggested in MOS transistor gates, as an alternative to SiO2. The advantage is thicker films, reducing simultaneously the tunnel current and the gate voltage. However, in practice, the performances of the devices are greatly reduced because of the presence of defects in the deposited films and the consequent reduction of the dielectric constant. A proper modeling of the mechanisms involved during deposition seems therefore necessary for an adequate design of the process. We are interested in HfO2 which is one of the potential candidates. Our objective is to develop a multi-scale modeling associating ab initio results with a Monte Carlo simulation. In this paper, we focus mainly on the ab initio investigation of chemical reactions between the substrate and the precursor molecules in the gas phase, used in the atomic layer epitaxy process. Several types of precursors and different surface configurations have been tested. The energies associated with these configurations will be discussed in order to determine the reaction paths and to estimate the corresponding energies.

5 General Workshop/Conference Announcements

5.1 Conference in Bristol, UK

1st Announcement
Order and disorder in solids: alloys, magnetism and superconductivity

A celebration of the contributions of Balazs Györffy to theories of the electronic structure of solids.

Bristol, 11-13 April, 2003

Background

Balazs Györffy has made major contributions in several areas of solid state physics, including: metallic alloys, metallic magnetism, superconductivity and relativistic quantum effects in solid state physics. This meeting marks the occasion of his 65th birthday. Workshop talks will encompass the current state of the art in all of the diverse fields in which Balazs has had a major contribution.

Dates: Friday 11 April to Sunday 13 April 2003.

Location

H H Wills Physics Laboratory, University of Bristol. (Note that the annual CMMP Conference will take place in Belfast 7-10 April 2003, and timings will allow participants to travel from Belfast to Bristol to attend both meetings.)

Registration Fee

A Registration Fee of £120 (£60 for students) will include coffees, lunches and conference banquet. Accommodation will be available in nearby hotels and university residences.

Speakers (tentative)

G M Stocks (Oak Ridge)
J B Staunton (Warwick)
O K Andersen (Stuttgart)
E K U Gross (Berlin)
H Ebert (Munich)
R West (Arlington)
A Georges (Saclay)

P Allen (SUNY)
W Butler (Alabama)
B Ginatempo (Messina)

Organising Committee

M A Alam, J F Annett, R Evans, W Temmerman, P Strange, J Staunton.

To receive further details email to Tracie.Anderson@bristol.ac.uk

REALISTIC THEORIES OF CORRELATED ELECTRON MATERIALS

A conference organized at KITP-Santa Barbara

November 18-22, 2002

Organizers: O. Andersen, A. Georges, G. Kotliar, A. Lichtenstein

This conference will focus on several classes of the strongly correlated electron materials, including: transition metals and their oxides, cuprate superconductors, rare earths, actinides and their compounds, as well as organic conductors. The emphasis will be put on key open issues in the physics of these various materials. Recent theoretical advances will also be a main theme of the conference, including methods combining many-body techniques and electronic structure calculations, as well as numerical methods addressing strong-coupling effects of electron-electron interactions.

CONFIRMED INVITED SPEAKERS INCLUDE:

D. Basov (UC-San Diego) "Optical properties of cuprate superconductors: an overview"

G. Blumberg (Lucent) - title to be announced -

J.C. Campuzano (Chicago) -title to be announced-

E. Dagotto (Florida State) " Nanoscale phase separation and colossal magnetoresistance"

A. Fujimori (Tokyo) "Material dependence of the band structure of cuprates, and its relation with Tc"

T. Giamarchi (Geneva) " Quasi one-dimensional organic conductors: dimensional crossovers and deconfinment transition" (tentative title)

B. Keimer (Stuttgart) "Magnetic Dynamics in Orbitally Degenerate Mott Insulators"

G. Sawatzky (UBC-Vancouver) -title to be announced-

S. Savrasov (NJIT) "Correlation effects in plutonium: a Dynamical Mean Field perspective" (tentative title)

F. Steglich (Dresden) -title to be announced-

H. von Lohneysen (Karlsruhe) -title to be announced-

HOW TO REGISTER

Attendance at the conference is limited. Registration can be filled out on the KITP web site:

http://www.itp.ucsb.edu/activities/cem_c02/?id=268

For further information about the scientific aspects of the conference and/or presenting new results, please feel free to contact Antoine Georges (georges@kitp.ucsb.edu).

For logistic details, please contact the KITP Administrative Coordinator, Sue Alemdar (sue@kitp.ucsb.edu).

International Conference on Materials for Advanced Technologies (ICMAT2003)

and

7th IUMRS International Conference in Asia (IUMRS-ICA2003)

SYMPOSIUM ON THEORY, MODELING AND SIMULATION

29 June - 4 July, 2003, Singapore

CALL FOR ABSTRACTS

The above Symposium on Theory, Modeling and Simulation will be held, in conjunction with the International Conference on Materials for Advanced Technologies (ICMAT 2003) and the 7th IUMRS International Conference in Asia (ICA 2003), from 29 June to 4 July in Singapore.

The objective of the symposium is to provide an international forum for discussion of a range of computational methods and their applications to materials science. It will bring together theorists and computational scientists from all over the world to the tropical garden, Singapore, to discuss the latest developments in computational techniques, to exchange ideas, and to interact with experimentalists. Contributions in all relevant areas, particularly in computational nanotechnology and nanoscale electronics, simulation of novel materials, and modeling techniques and applications, are welcome.

TOPICS OF INTEREST

Topics covered will include, but are not limited to, the following:

Computational Nanotechnology & Nanoscale Electronics
Synthesis of nanoscale objects
Self-organization
Electronic properties of nanoscale objects
Optical and transport properties
Thermal and mechanical stability
Simulation of Novel Materials
Ferroelectrics, ferroelastics, piezoelectrics, complex oxides
Magnetic materials
Polymeric systems
Metals
Fullerene structures

Modeling Techniques and Applications
First-principles, atomistic and continuum modeling
Multiscale modeling
Defects
Microstructure
Kinetics
Mechanical and transport properties

INVITED SPEAKERS (Tentative & Partial)

O. K. ANDERSEN, Max Planck Institute, Germany
R. CAR, Princeton University, USA
G. CEDER, MIT, USA
D. M. CEPERLEY, University of Illinois, USA
T. FRAUENHEIM, University of Paderborn, Germany
M. HEAD-GORDON, UC Berkeley, USA
H. GUO, McGill University, Canada
Y. KAWAZOE, Tohoku University, Japan
P. GUMBSCH, Max Plank Institute, Germany
M. L. KLEIN, University of Pennsylvania, USA
V. KUMAR, Dr. Vijay Kumar Foundation, India
L. W. M. LAU, Chinese Univ. of Hong Kong, China
S. S. LIAN, National Taiwan University, Taiwan
S. G. LOUIE, UC Berkeley, USA
M. PARRINELLO, Swiss Centre for Scientific Computing, Switzerland
M. C. PAYNE, Cambridge, UK
D. SALAHUB, University of Montreal, Canada
M. SCHEFFLER, FHI, Germany
A. SUTTON, University of Oxford, UK (tentative)
K. TERAKURA, AIST, Japan (tentative)

IMPORTANT DATES

Abstract submission: December 15, 2002
Acceptance of abstracts: January 15, 2003
Early registration: March 31, 2003
Full length manuscript: June 1, 2003

PROCEEDINGS

The proceedings of the symposium will be published in Computational Materials Science. The normal journal reviewing process applies. Information about abstract and manuscript Preparation will be made available later.

FURTHER INFRMATION

For further information, visit the conference web site

http://www.mrs.org.sg/icmat2003

or contact any of the following organizers

Yuan Ping Feng, National Univ. of Singapore, phyfyp@nus.edu.sg
Michael Philpott, National Univ. of Singapore, mashead@nus.edu.sg
Ping Wu, Inst. High Performance Computing, wuping@ihpc.nus.edu.sg
Kan Chen, National Univ. of Singapore, cscchenk@nus.edu.sg
David J. Srolovitz, Princeton University, srol@priceton.edu

Workshop on the Fundamental Physics of Ferroelectrics: FERRO 2003

2-5 February, 2003

"Fundamental Physics of Ferroelectrics" returns to its original location in 2003. The workshop will be held at the Williamsburg Woodlands Conference Center in Colonial Williamsburg, U.S.A. The workshop is intended to serve as a forum for the discussion of fundmental aspects of the physics of ferroelectricity and ferroelectric materials, including both theory and experiment. The conference is being organized by P.K. Davies (University of Pennsylvania) and D.J. Singh (Naval Research Laboratory).

The scientific advisory committee consists of:

Laurent Bellaiche, University of Arkansas, U.S.A.
R. Blinc, J. Stefan Institute, Slovenia
D.J. Chadi, NEC Research Institute, U.S.A.
Haydn H. Chen, University of Illinois, U.S.A.
Ronald E. Cohen, Geophysical Laboratory, U.S.A.
Takeshi Egami, University of Pennsylvania, U.S.A.
Marc Fontana, Metz University, France
Henry Krakauer, College of William and Mary, U.S.A.
Beatriz Noheda, Brookhaven National Laboratory, U.S.A.
P.M. Gehring, NIST, Gaithersburg, U.S.A.
Raffaele Resta, University of Trieste, Italy
George A. Samara, Sandia National Laboratory, U.S.A.
Ekhard Salje, University of Cambridge, U.K.
James F. Scott, University of Cambridge, U.K.
Jean Toulouse, Lehigh University, U.S.A.

Further details will be posted on the web site:

`http://cst-www.nrl.navy.mil/~singh/ferro2003`

5.5 Winter School in France

"From Elasticity to plastic flow in condensed media"

February 3-15, 2003

Les Houches, France

General information about the programme and registration can be found at

`http://consoude.ujf-grenoble.fr/leshouches2003/conference_homepage.html` .

The Organizing Committee

Christiane Caroli
Chaouqi Misbah
Philippe Peyla

International Workshop on
X-RAY SPECTROSCOPIES OF MAGNETIC SOLIDS 2002
(XRMS-02)
December 7-8, 2002
Institute of Solid State & Materials Research (IFW), Dresden, Germany

The XRMS-02 Workshop is devoted to current experimental and theoretical advances in the field of x-ray spectroscopy of magnetic materials. Topics of the Workshop include:

- magnetic circular and linear dichroism
- spin-resolved photoemission
- x-ray imaging of magnetic microstructures
- time-resolved studies of magnetic processes
- x-ray magneto-optics
- Auger electron spectroscopy
- Compton scattering

List of speakers (preliminary):

Dimitri Arvanitis (Uppsala)	Julio Camarero (Madrid)
Carsten Detlefs (Grenoble)	Sarnjeet Dhesi (Grenoble)
Manfred Faehnle (Stuttgart)	Pietro Gambardella (Lausanne)
Jose Goulon (Grenoble)	Young-June Kim (Brookhaven)
Wolfgang Kuch (Halle)	Frithjof Nolting (Villingen)
Oliver Rader (Berlin)	L. Hao Tjeng (Cologne)
Gerrit van der Laan (Daresbury)	

For more information, see the webpage:

http://www.ifw-dresden.de/xrms02

Abstract deadline: November 15, 2002

Organizers:

Peter M. Oppeneer & Claus M. Schneider
Leibniz-Institute of Solid State & Materials Research
Helmholtzstr. 20, D-01069 Dresden, Germany
Phone: +49-351-4659-352 or -666, Fax -745
E-mail: XRMS02@ifw-dresden.de

5.7 IWOSMA2 Workshop

2nd International Workshop on Orbital And Spin Magnetism of Actinides (IWOSMA2)

October 13 -15, 2002, Berkeley

Chair: J.G. Tobin, LLNL

Co-Chair: D.K. Shuh, LBNL

Web-site: http://www.iwosma.org

The 2nd International Workshop on Orbital and Spin Magnetism in Actinides will take place at the Claremont Hotel in Berkeley, CA on October 13 -15, 2002. The invited speaker list includes participants from Russia, France, Germany, Sweden, Great Britain and the Czech Republic. Below is the Meeting Agenda.

Proposed Agenda for IWOSMA2

Sunday, October 13

5:00 PM Reception and Opening Poster Session 8:00 PM End

Monday, October 14

8:00 AM Welcome

8:10 AM Session I: Theoretical Overview and Recent Developments

8:10 AM B. Johansson, "Magnetic, Structural and Electronic Relationships between the Lanthanide and Actinide Elements"

8:50 AM G. Kotliar, "Dynamical Mean Field Theory of Elemental Plutonium"

9:30 AM A.McMahan, "Thermodynamic and spectral properties of compressed Ce calculated by the merger of LDA and DMFT"

10:10 AM Break

10:30 AM Session II: Photoelecton Spectroscopy of Pu and Pu Mat'ls

10:30 AM T. Gouder, "5f Localization in Ultrathin Pu Layers"

11:10 AM J. Joyce, "Electronic Structure of Pu and Pu Compounds from PES"

11:50 PM Lunch

1:00 PM J. Tobin, "A New Paradigm for the Determination of 5f Electronic Structure using Spin-Dependent Photoelectron Spectroscopy"

1:40 PM G. van der Laan, "Core-level photoemission spectra as a tool to assess the 5f electron

localization of alpha and delta-like Pu"

2:20 PM Session III: Poster Viewing with Refreshments

4:00 PM Session IV: Resistivities and Susceptibilities

4:00 PM J.-M. Fornier, "Magnetic properties of PuAm solid solutions : evidence for a Curie-Weiss behavior and aging effects"

4:40 PM L. Havela, "Non-Fermi Liquid Behavior in a Band Metamagnet UcoAl"

5:20 PM M. Fluss, "Temp Dependent Properties of Defects from Ion-Irradiation in Pu(Ga)"

6:00 PM End

7:00 PM Dinner
W. Nellis, " Metallization of Hydrogen"

Tuesday, October 15

8:00 AM Session V: X-ray and Neutron Measurements, Analysis and Simulations

8:00 AM N. Edelstein, "Interplay of the spin-orbit and crystal field interactions of fn ions in crystals"

8:40 AM G. Lander, "NpO2 : resonant x-ray scattering casts new light on an old problem"

9:20 AM K. McEwen, "Quadrupolar and magnetic phase transitions in UPd3"

10:00 AM Break

10:30 AM M. Brooks, "Theory of Ground State Spin and Orbital Moments with Screened Exchange Interactions"

11:10 AM L. Soderholm, "Correlated Electron Behavior in a Eu-exchanged W-O cluster"

11:50 PM Lunch

1:00 PM Session VI: Pu Theory

1:00 PM P. Soderlind, "Density-functional investigation of magnetism in delta-Pu"

1:40 PM J. Wills, "A mixed-level model of orbital and spin correlation in actinide materials"

2:20 PM Break

2:50 PM B. Sadigh, "First-Principles Calculations of the alpha and delta phases in Pu and Pu-Ga"

3:30 PM A. Kutepov, "The ab-initio magnetic moments of alpha-plutonium"

4:10 PM Session VII: Workshop Summary and Discussion

5:00 PM End

First Announcement

International Conference on Nanoelectronics

Chair: Vladimir Falko (Lancaster University)

Co-Chairs: Colin Lambert (Lancaster University), Walter Temmerman (Daresbury Laboratory)

Web-site: http://www.lancs.ac.uk/users/esqn/nanoelectronics/

This multi-disciplinary conference will bring together leading researchers in the rapidly developing field of nanoelectronics.

Topic will include:

Ab initio modelling of transport, materials and interfaces;

molecular-scale electronics and atomic contacts;

correlations in quantum dots, wires and rings;

quantum transport with correlations;

quantum transport and quantum noise;

spin-dependent transport and control;

quantum manipulation and the physics of qubits;

proximity effects and hybrid structures;

nano-electronic devices and materials.

The conference will be held on January 4-9, 2003, at Lancaster University, UK. A partial list of invited speakers is shown below. Although many of the presentations will be invited talks, contributed talks and posters are welcome and participation by young researchers is particularly encouraged. Details of abstract submission, as well as registration and accommodation are available from the conference web-site.

Partial List of Invited Speakers:

Carlo Beenakker(Leiden)
Fabio Beltram (Pisa)
Peter Beton (Nottingham)
Stefan Blügel (Julich)

Arne Brataas (Trondeim)
Marcus Büttiker (Geneva)
Bogdan Bulka (Poznan)
Venkat Chandrasekhar (Northwestern)
Per Delsing (Chalmers)
Andre Geim (Manchester)
Klaus Ensslin (ETH Zurich)
Rosario Fazio (Pisa)
Albert Fert (Orsay)
Mike Finnis (Belfast)
Bryan Gallagher (Nottingham)
Leonid Glazman (Minneapolis)
Pertii Hakonen (LTL Espoo)
Rolf Haug (Hannover)
David Haviland (Stockholm)
Frank Hekking (Grenoble)
Paul Kelly (Twente)
Jrg Kotthaus (Munich)
Mariusz Krawiec (Bristol)
Laurent Lévy (LCMI Grenoble)
Igor Lerner (Birmingham)
Poul Lindelof (Copenhagen)
Daniel Loss (Basel)
Allan MacDonald * (Austin)
Dominique Mailly (LPN Marcoussis)
Laurens Molenkamp* (Wrzburg)
Hans Mooij (Delft)
Yuli Nazarov (Delft)
Bernard Pannetier (CRTBT Grenoble)
Francois Peeters (Antwerp)
Victor Petrashov (Royal Holloway)
Jean-Louis Pichard (Saclay)
Angel Rubio (San Sebastian)
Jan von Ruitenbeek (Leiden)
Gerd Schön (Karlsruhe)
Christian Schönenberger (Basel)
Robert Shekhter (Chalmers)
Andrew Shields (Toshiba Cambridge)
Maurice Skolnick (Sheffield)
Uri Sivan (Technion)
Ben Simons (Cambridge)
Hideaki Takayanagi (NTT Atsugi)
Cristian Urbina (Saclay)

Lieven Vandersypen (Delft)
Bart van Wees (Groningen)
Jurgen Weis (MPI-Stuttgart)
David Williams (Hitachi Cambridge)
Amir Yacoby (Weizmann Inst.)
Nikolai Zhitenev (Bell Labs - Lucent)

6 General Job Announcements

Postdoctoral Position in Computational Electronic Structure Theory

Rutgers University

A post-doc opening is expected to become available in the group of Prof. David Vanderbilt at Rutgers University. The preferred starting date would be in February or March 2003. The primary focus of the work will be on first-principles based theoretical studies of ferroelectric and related materials. Familiarity with ab-initio density-functional methods is essential.

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

Prof. David Vanderbilt
Department of Physics and Astronomy
Rutgers University
136 Frelinghuysen Road
Piscataway, NJ 08854-8019, USA

Phone: (732) 445-2514
Fax: (732) 445-4400
Email: dhv@physics.rutgers.edu
`http://www.physics.rutgers.edu/~dhv`

Two PhD Studentships, University of Nebraska-Lincoln
"Modelling of novel spin-electronic devices"

Two PhD studentships are available at the Physics Department of the University of Nebraska-Lincoln (UNL) in theory of spin-dependent transport and in micromagnetics of novel magnetoresistive devices. In the first project first-principle and tight-binding models will be used to design structures and materials for spin-electronic applications. This project is funded by Seagate Research, Pittsburgh, PA, and will be performed in a close collaboration with experimental and theoretical groups at Seagate Research. The second project will involve micromagnetic modeling to study the influence of the atomic structure and temperature on magnetization reversal in magnetic nanostructures. This area of research is relevant to interests of magnetic recording and storage industries and also to experimental groups at the UNL. Strong background in solid state theory and programming skills are required for these positions. Candidates should send (preferably by e-mail) the curriculum vitae and names of two references to

Evgeny Tsymbal
Associate Professor in Physics
Department of Physics and Astronomy
University of Nebraska-Lincoln
Lincoln, NE 68588-0111
Phone: (402) 472-2586
Fax: (402) 472-2879
E-mail: tsymbal@unl.edu

Computational Chemist or Physicist/ Material Scientist with a extensive background in computing
One permanent post at Daresbury Laboratory, UK

The Data Management Group of the CLRC e-Science centre is looking for a skilled computational chemist, physicist or material scientist with extensive computing knowledge and an interest in Grid developments to work on a variety of atomistic simulation software packages based on both empirical potential and first principles methodologies. The initial project is to work with leading groups in the UK to build a database of computational and experimental derived properties. The post holder will be required to support the development of the necessary Grid computing environment.

The two initial projects: the NERC funded 'Environment from the Molecular Level' and the EPSRC funded 'e-Science techniques for the simulation of complex materials'

(see http://www.e-science.clrc.ac.uk/Activity/ACTIVITY=DataPortal for more details),

will focus their research on the following topics: Surface growth and dissolution, Sulphide surfaces, Organic molecule and metal adsorption on silicates, Radiation damage/encapsulation, combinatorial materials science and polymorph of pharmaceutical crystals. We expect to use amongst others codes like: `DL_POLY` , Siesta and QMC and will be closely working with the developers of these codes.

The position will provide an excellent opportunity to apply and extend your skills in an exciting and rapidly developing area, which will drive scientific and commercial computing over the next decade. The successful applicant will play a leading role in helping to build the UK Grid and will have the opportunity to work closely with world class scientists exploiting the Grid to solve some of the most challenging scientific problems. There will be good opportunities for further training and to attend international conferences.

The applicant will be expected to be educated to degree level. Successful applicants will have experience of materials simulation, an ability to collaborate extensively and excellent computer science skills as well as be flexible, resourceful, good communicators and able to work effectively in a team.

Starting Salary will be up to 25,510 GBP on a salary scale of 20,410 GBP to 28,060 GBP depending on relevant experience. An index linked pension scheme, flexible working hours and a generous leave allowance are offered.

Application forms can be obtained from HR Division, Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD. Telephone (01925) 603114 (answerphone) or email recruit@dl.ac.uk quoting reference number VND2286R.

Applications should be returned by 10th October 2002.

7 Abstracts

Magnetic circular dichroism in $2p3p3p$ resonant photoemission from ferromagnetic Ni in perpendicular geometry across the L_3 edge

M. Taguchi and G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

Abstract

We present calculations for the magnetic circular dichroism (MCD) in the $3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 3p^4 3d^{n+1}\varepsilon$ photoemission process in resonance with the $2p$ x-ray absorption from ferromagnetic Ni in perpendicular geometry (PG). The calculations are based on a coherent second-order optical process taking into account intra-atomic multiplet and configuration interaction. The MCD in PG at the L_3 edge is found to be in excellent agreement with previous experimental results. At the excitation energy of the 4 eV and 6 eV satellites the predicted MCD is strongly different which should permit to assess the angular dependence of the intra-atomic Coulomb interaction.

(Submitted to Phys. Rev. B)
Contact person: g.vanderlaan@dl.ac.uk

Soft x-ray magnetic speckles from a nanostructured FePd wire

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A. Marty
Département de Recherche Fondamentale sur la Matière Condensée, Service de Physique des Matériaux et Microstructures, 17, Rue des Martyrs, F-38054 Grenoble Cedex 9, France

Abstract

We have recorded magnetic speckle patterns of unprecedented quality on a tiny sample using soft x-ray resonant magnetic scattering in reflection geometry. This geometry is well suited to the study of epitaxial thin films. The microscopic object consisted of an FePd wire with transversal stripe domains of alternatingly up and down magnetization. Sharp magnetic superstructure peaks reflect the domain periodicity, whereas the magnetic speckles give access to the domain morphology. A high degree of coherence has been obtained ($\beta = 0.85$) as evidenced from the strong observed intensity fluctuations.

(Submitted to Phys. Rev. B)
Contact person: g.vanderlaan@dl.ac.uk

Systematic theoretical study of the spin and orbital magnetic moments of 4d and 5d interfaces with Fe films

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H. Ebert
University of Munich, D-81377 Munich, Germany

Abstract

Results of *ab initio* calculations using the relativistic Local Spin Density theory are presented for the magnetic moments of periodic $5d$ and $4d$ transition metal interfaces with bcc Fe(001). In this systematic study we calculated the layer-resolved spin and orbital magnetic moments over the entire series. For the Fe/W(001) system, the Fe spin moment is reduced whilst its orbital moment is strongly enhanced. In the W layers a spin moment is induced, which is antiparallel to that of Fe in the first W layer but parallel to Fe in the subsequent W layers. The W orbital moment does not follow the spin moment. It is aligned antiparallel to Fe in the first two W layers and changes sign in the third W layer. The calculations show that the oscillatory behavior of the W spin moment is in phase with the charge modulation over the W layers. Small changes in the band filling can lead to a reversal of the orbital moment of the first W layer. The trend in the spin and orbital moments over the $4d$ and $5d$ series for multilayers is quite similar to previous impurity calculations. These observations strongly suggest that these effects can be seen as a consequence of the hybridization between $5d$ ($4d$) and Fe which is mostly due to band filling, and to a lesser extent geometrical effects of either single impurity or interface.

(Submitted to Phys. Rev. B)
Manuscripts available from: W.M.Temmerman@dl.ac.uk

Ab initio charge, spin and orbital energy scales in manganites

R. Tyer[1,2], W.M. Temmerman[1], Z. Szotek[1], A. Svane[3], L. Petit[3], G.A. Gehring[2]

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[2] *Department of Physics and Astronomy, University of Sheffield, Sheffield, S3 7RH, UK*

[3] *Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus, Denmark*

Abstract

The first-principles SIC-LSD theory is utilized to study electronic, magnetic and orbital phenomena in manganites. For both $CaMnO_3$ and $LaMnO_3$ the correct ground states are found, which in the latter is antiferro orbitally ordered with the spin magnetic moments antiferromagnetically aligned. Jahn-Teller energies are obtained which are larger than energy differences between magnetic structures. The study correctly describes the pressure induced delocalization of an e_g electron in $LaMnO_3$.

(Submitted to Phys. Rev. Lett.)

Manuscripts available from: W.M.Temmerman@dl.ac.uk

Computer Simulation Studies of Ceria-based Oxides

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Abstract

Computer modelling techniques are now well-established tools in the field of materials chemistry, and have been applied successfully to studies of structures, energetics and dynamics of a wide range of solids at the atomic level. A major theme of modelling work has been the strong interaction with experimental studies, which is evolving in the direction of increasingly complex systems. This review addresses recent trends and progress in the use of such computational techniques in the investigation of the defect, transport and surface properties of ceria (CeO2)-based materials.

(in Catalysis by Ceria and Related Materials (Ed. by A. Trovarelli), Imperial College Press, London (2002))

Contact person: m.islam@surrey.ac.uk

Computer Modelling of Defects and Transport in Perovskite Oxides

M.S. Islam

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Abstract

This paper presents recent investigations of the defect, ion transport and surface properties of ABO3 perovskite-structured oxides using advanced computer simulation techniques. The principal methodologies are outlined which include techniques based upon energy minimisation and interatomic potentials, and quantum mechanical methods. The scope of computational studies of perovskites is illustrated by contemporary work on the topical systems LaGaO3, LaCoO3 and CaZrO3; the properties examined include mechanisms of oxygen ion migration, dopant-defect association, dynamics of proton diffusion and, finally, structures of oxide surfaces.

(Solid State Ionics (2002), in press)

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Spin-filter effect in metallic nanowires

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I. Mertig
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Abstract

We present ab-initio calculations for metallic nanowires with a diameter of few atoms. The electronic structure is calculated using the screened Korringa Kohn Rostoker (KKR) Green's function method, while electronic transport properties are obtained using a Green's function formulation of the Landauer formalism. We focus on the effect of scattering due to transition metal impurities on the conductance of a Cu wire. For a single defect, our results show a reduction of the transmission for energies at the impurity d state and due to the spin polarization conductance is different for the two spin directions causing a spin filter effect. For a defect pair, quantum interference effects lead to a complicated energy dependence of the conductance.

(Submitted to Phys. Rev. B)
Manuscripts available from: papanikolaou@ims.demokritos.gr

The Valency of Rare Earths in RIn_3 and RSn_3: *Ab initio* Analysis of Electric-Field Gradients

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Abstract

In RIn_3 and RSn_3 the rare earth (R) is trivalent, except for Eu and Yb that are divalent. This was experimentally determined in 1977 by Perturbed Angular Correlation (PAC) measurements of the electric-field gradient on a ^{111}Cd impurity. At that time, the data were interpreted using a point charge model, which is now known to be unphysical and unreliable. This makes the valency determination potentially questionable. We revisit these data, and analyze them using *ab initio* calculations of the electric-field gradient. From these calculations, the physical mechanism that is responsible for the influence of the valency on the electric-field gradient is derived. A generally applicable scheme to interpret electric-field gradients is used, that in a transparent way correlates the size of the field gradient with chemical properties of the system.

(Submitted to Phys. Rev. B)
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Quasiparticle Calculations for Point Defects on Semiconductor Surfaces

Magnus Hedström, Arno Schindlmayr and Matthias Scheffler
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Abstract

We discuss the implementation of quasiparticle calculations for point defects on semiconductor surfaces and, as a specific example, present an *ab initio* study of the electronic structure of the As vacancy in the +1 charge state on the GaAs(110) surface. The structural properties are calculated with the plane-wave pseudopotential method, and the quasiparticle energies are obtained from Hedin's *GW* approximation. Our calculations show that the $1a''$ vacancy state in the band gap is shifted from 0.06 to 0.65 eV above the valence-band maximum after the self-energy correction to the Kohn-Sham eigenvalues. The *GW* result is in close agreement with a recent surface photovoltage imaging measurement.

(submitted to: phys. stat. sol. (b))
Contact person: Magnus Hedström (hedstrom@fhi-berlin.mpg.de)

Sub-surface Oxygen and Surface Oxide Formation at Ag(111): A Density-functional Theory Investigation

Weixue Li[1], Catherine Stampfl[1,2], Matthias Scheffler[1]
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[2] *Department of Physics and Astronomy, Northwestern University, Evanston, Il. 60208-3112, USA*

Abstract

To help provide insight into the remarkable catalytic behavior of the oxygen/silver system for heterogeneous oxidation reactions, purely sub-surface oxygen, and structures involving both on-surface and sub-surface oxygen, as well as oxide-like structures at the Ag(111) surface have been studied for a wide range of coverages and adsorption sites using density-functional theory. Adsorption on the surface in fcc sites is energetically favorable for low coverages, while for higher coverage a thin surface-oxide structure is energetically favorable. This structure has been proposed to correspond to the experimentally observed (4×4) phase. With increasing O concentrations, thicker oxide-like structures resembling compressed $Ag_2O(111)$ surfaces are energetically favored. Due to the relatively low thermal stability of these structures, and the very low sticking probability of O_2 at Ag(111), their formation and observation may require the use of atomic oxygen (or ozone, O_3) and low temperatures. We also investigate diffusion of O into the sub-surface region at low coverage (0.11 ML), and the effect of surface Ag vacancies in the adsorption of atomic oxygen and ozone-like species. The present studies, together with our earlier investigations of on-surface and surface-substitutional adsorption, provide a comprehensive picture of the behavior and chemical nature of the interaction of oxygen and Ag(111), as well as of the initial stages of oxide formation.

(submitted to: Phys. Rev. B)
Contact person: Weixue Li (wxli@phys.au.dk)

Effect of a humid environment on the surface structure of $RuO_2(110)$

Qiang Sun, Karsten Reuter and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin-Dahlem, Germany

Abstract

Combining density-functional theory and thermodynamics we compute the phase diagram of surface structures of rutile $RuO_2(110)$ in equilibrium with water vapor in the complete range of experimentally accessible gas phase conditions. Through the formation of hydroxyl or water-like groups, already lowest concentrations of hydrogen in the gas phase are sufficient to stabilize an oxygen-rich polar oxide termination even at very low oxygen pressure.

(submitted to: Phys. Rev. B)
Contact person: Qiang Sun (sun@fhi-berlin.mpg.de)

Adhesion of Cu and Al_2O_3 from First Principles

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Abstract

Structures and energetics of various, plausible realizations of the $Al_2O_3(0001)/Cu(111)$ interface have been studied by density-functional theory. The oxygen-terminated interface is found to be relatively strong with a work of separation (W_{sep}) of 7.03 J/m^2. For hydrogen-rich (e.g. moist) conditions we obtained that the interface will accommodate about 1/3 of a monolayer of hydrogen. This lowers W_{sep} to 4.72 J/m^2, which is, however, still larger than the corresponding value for bulk Cu, implying that fracture in such system will occur in the Cu region, consistent with fracture toughness experiments. We also studied the initial stages of Cu and Al growth on the H-stabilized oxygen-terminated $Al_2O_3(0001)$ surface. While a monolayer of Al already completely dissociates the interfacial O-H group, a monolayer of Cu leaves it intact. If, for a thick Cu film, such full hygrogen layer were maintained, the resulting metastable interface is very weak with $W_{sep} = 0.63$ J/m^2.

(submitted to: J. American Ceramic Society)
Contact person: Xiao-Gang Wang (xwang@gmr.com)

Ab-initio determination of the localized/delocalized f-manifold in UPd_2Al_3

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R. Tyer
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United Kingdom
and *Department of Physics and Astronomy, University of Sheffield,*
Sheffield, S3 7RH, United Kingdom

Abstract

The electronic structure of UPd_2Al_3 is described using the self-interaction corrected local-spin-density approximation to density functional theory. The groundstate is found to be characterized by the coexistence of localized (f^2) and delocalized U f electrons, in agreement with experimental evidence. We observe significant difference in electronic structure between UPd_2Al_3 and UPt_3. Even though a trend towards localization exists in UPt_3, the total energies and the density of states at the Fermi level favor a groundstate with localized f^1, rather than f^2 U ions.

(Europhysics Letters : submitted)
Manuscripts available from: svane@phys.au.dk

Linear hydrocarbons adsorbed in the acid zeolite gmelinite at 700 K. Ab initio molecular dynamics simulation of hexane and hexene

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[1] *Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, Sensengasse 8, A-1090 Wien, Austria;* [2] *Totalfinaelf, Centre Européen de Recherche et Technique, B. P. 27, F-76700 Harfleur, France;* [3] *Institut Français du Pétrole, F-92852 Rueil-Malmaison Cedex, France*

Abstract

First-principles molecular dynamics simulations are performed to sample the behavior of linear hydrocarbons within the acid zeolite gmelinite at high temperature. The analysis of the trajectories, the time-development of the bond lengths and simulated IR spectra are presented for both neutral and protonated molecules. The acid proton shows no affinity towards paraffin and slightly increased affinity towards the double bond of the olefin. No spontaneous protonation of the olefin is observed. The simulation of the protonated linear C6H13+ molecule shows that the protonated species is stabilized within the zeolite framework and no collapse to the neutral molecule occurs. No cracking or isomerization event is observed. The protonated molecule shows rather high mobility accompanied by a series of hydride transfers along the chain of the molecule. The transfer of the H-atom leads to a relocation of positive charge. The relocation is correlated to the position of the Al-site in the zeolite framework. In the simulated IR spectra we observe no distinctive feature evidencing the existence of the protonated species.

J. Catal, 205 (2002) 147

Preprints available from: lubomir.benco@univie.ac.at

Extra-framework aluminum species in zeolites. Ab initio molecular dynamics simulation of gmelinite

L. Benco[1], T. Demuth[1], J. Hafner[1], F. Hutschka[2], H. Toulhoat[3]

[1] *Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, Sensengasse 8, A-1090 Wien, Austria;* [2] *Totalfinaelf, Centre Européen de Recherche et Technique, B. P. 27, F-76700 Harfleur, France;* [3] *Institut Français du Pétrole, F-92852 Rueil-Malmaison Cedex, France*

Abstract

The dynamical behavior of extra framework aluminum particles (EFAL) in zeolites has been investigated using a first-principles molecular dynamics technique. Small clusters of hydrated aluminum hydroxide $Al(OH)_3(H_2O)_3$ and $Al(OH)_3(H_2O)$, are located both in the main channel and in the cage. The simulation of the hexacoordinated cluster at T = 300 K shows an overcoordination of the central atom and a release of H_2O molecules. When placed in the main channel both the EFAL and the non-coordinated H_2O molecules are mobile. When placed in the cage, a network of hydrogen bonds is established occluding the EFAL and suppressing its mobility. The basic character of the EFAL causes an exchange of Brønsted acid protons between the zeolite and the EFAL particle. In a high-acidity zeolite a multiple, simultaneous proton exchange is observed leading to a separation of charges ($EFAL^{2+}$, $zeolite^{2-}$). The calculated stretching OH frequencies of the EFAL are $\sim$60 cm^{-1} higher than those of the Brønsted OH in good agreement with IR measurements.

J. Catal, 209 (2002) 480

Preprints available from: lubomir.benco@univie.ac.at

Ab-initio density functional investigation of the (001) surface of mordenite

T. Bucko, L. Benco, Th. Demuth and J. Hafner

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Abstract

Structural and acidic properties of the (001) surface of mordenite have been studied using density functional theory including generalized gradient corrections to the exchange-correlation functional. Our calculations, in agreement with experimental results, show that the surface structure of mordenite differs only moderately from the bulk structure, no reconstruction of the surface has been found. Part of the terminal silanol groups form weak hydrogen bonds with other framework oxygen sites, the lengths of hydrogen bonds vary in the range 1.9 to 2.6 Å depending on the position of the Al site. The OH-stretching frequencies for various acid sites in the mordenite framework have been calculated. In agreement with experiment, calculated OH-stretching frequencies of terminal silanol groups are shifted by about 100 cm^{-1} with respect to the Brønsted acid sites. Those silanol groups whose OH–stretching frequencies are modified by the presence of hydrogen bonds are shown to absorb in the region typical for the Brønsted acid sites.

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8 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Ferromagnet/Superconductor Heterostructures" by Mariusz Krawiec

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Ferromagnet/Superconductor Heterostructures

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Abstract

Some of the properties of the ferromagnet/superconductor proximity heterostructures are discussed. The particular emphasis is put on the physics of Andreev reflections featuring in unusual thermodynamic and transport properties of the system. These are: presence of the Andreev bound states, oscillatory behavior of the pairing amplitude, density of states and superconducting critical temperature, when the thickness of the ferromagnet is varied. They can produce spontaneous spin polarized currents flowing parallel to the interface, generating a magnetic field. They are responsible for a realization of a new state in such system, which is very similar to Fulde - Ferrell - Larkin - Ovchinnikov ($FFLO$) state predicted for an exchange split bulk superconductor. Some experiments, giving a rather surprising results may be explained in terms of $FFLO$ - Andreev bound states.

1 Introduction

Seventy years ago the proximity effect was observed experimentally [1] for the first time. Measuring the resistance of the normal metal (NM), placed between two superconductors (SC), one observed that superconductivity entered the normal metal, causing the resistance to vanish.

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Such a penetration of the superconducting properties into a normal state material is known now as a *proximity effect*.

The superconductivity is characterized by the order parameter $\Delta(\mathbf{r})$ which is related to the pairing amplitude $\chi(\mathbf{r})$ ($\Delta(\mathbf{r}) = g\chi(\mathbf{r})$, $g \neq 0$ only in SC). Physically the square of the pairing amplitude is the density of paired electrons. Unlike $\Delta(\mathbf{r})$, $\chi(\mathbf{r})$ can extend into a normal metal in contact with a superconductor, leading to the proximity effect. First theoretical studies, using these arguments, have been done in early sixties [2]. Roughly at the same time the Andreev reflection process was proposed [3]. According to it, an impinging electron (with energy less than SC gap) on the NM/SC interface is reflected as a hole, and the Cooper pair is created in superconductor. These processes allow for the transfer of $2e$ charge even though there are no quasiparticle states available. From this point of view the pairing amplitude can be regarded as a density of the correlated electron-hole pairs in the normal metal. So one can say that proximity effect and Andreev reflections are two sides of the same phenomenon. The effect has been extensively studied and is rather well understood by now [4]. The properties of such material under proximity are strongly affected. For example the system is able to carry the supercurrent, density of states posses a gap and the tunneling characteristics are modified.

When the normal metal is replaced by a ferromagnet (FM), another energy scale enters the problem, namely the exchange splitting which is related to the spin polarization of the electrons. It makes the the physics of the proximity systems much more rich [5, 6]. Such proximity effect between ferromagnet and superconductor is less well understood. Moreover, recently it has become possible to fabricate high quality FM/SC heterostructures [7]-[10] making these materials very attractive from point of view of scientific interest, as they allow for studying the interplay between magnetism and superconductivity [11] as well as of device applications in various areas of technology like magnetoelectronics [12, 13] for example.

It is widely accepted that ferromagnetism and superconductivity are two antagonistic phenomena, so one could expect that the proximity effect in FM/SC system should be suppressed. Indeed, the one can argue that in ferromagnet there are different numbers of spin-up (majority) $n_\uparrow$ and spin-down (minority) $n_\downarrow$ conduction channels, and due to the fact that incident and reflected particles occupy different spin bands, only a fraction $n_\downarrow/n_\uparrow$ of majority particles can be Andreev reflected [14]. Such suppression of the Andreev conductance has been observed experimentally in the structures consisting of metallic ferromagnets and classical (BCS) superconductors [15, 16] as well as in the colossal magnetoresistance materials in contact with high-T_c (d-wave) superconductors [17].

On the other hand if an exchange field acts on the Cooper pairs, one would expect that either it is too weak to break the pair, or it leads through the first order phase transition to the normal (ferromagnetic) state. However when a Cooper pair is subjected to the exchange field, it acquires a finite momentum and for certain values of the exchange splitting a new superconducting state is realized, known as *Fulde - Ferrell - Larkin - Ovchinnikov* ($FFLO$) state [18, 19]. Interestingly such state features a spatially dependent order parameter.

Similar oscillations of the pairing amplitude have been predicted [20]-[23] in ferromagnet/superconductor proximity systems. It turns out that these oscillations are responsible for the oscillatory behavior of the SC critical temperature T_c, first experimentally observed by Wong *et al.* [24], and the

density of states [25] as the thickness of the FM slab is varied. In fact, the oscillations of the T_c in FM/SC multilayers can be also explained in terms of the effective π-junction behavior [21]. It was shown that at specific FM thickness the Josephson coupling between two SC layers can lead to a junction with an intrinsic phase (of the order parameter) difference $\delta\varphi = \pi$, which exhibits a higher T_c than the ordinary one ($\delta\varphi = 0$). The π-junction effect has been originally proposed by Bulaevskii *et al.* [26] to arise in the tunnel barriers containing magnetic impurities. Later on it has been shown that π-junction may exist in both ferro- and antiferromagnetic/superconductor multilayers [27]. It was also suggested that the π-junction can be realized in high-T_c superconducting weak links [28], where the SC order parameter changes its sign under $\pi/2$ rotation. This has tremendous consequences as it leads to many important effects [29, 30], like: the zero energy Andreev states, zero-bias conductance peaks, large Josephson current, time reversal symmetry breaking, paramagnetic Meissner effect and spontaneously generated currents.

From the point of view of the present paper the important issue is the formation of the Andreev bound states in FM/SC proximity system. The Andreev states arise due to the fact that the quasiparticles of the ferromagnet participating in the Andreev reflections move along closed orbits. Such states have been first studied by de Gennes and Saint-James [31] in the insulator/normal metal/superconductor ($I/NM/SC$) trilayer. The energies of these states are always smaller that SC gap Δ and symmetrically positioned around the Fermi level. They strongly depend on the geometry of the system as well as on the properties of the interfaces. In high-T_c (d-wave) superconductors, these states can be shifted to zero energy, due to the specific form of the symmetry of the order parameter [32], thus indicating π-junction behavior in the system. Naturally, such Andreev states can also arise in the $I/FM/SC$ heterostructures. Moreover, it is possible to shift the energies of these states changing the exchange splitting, as was first demonstrated by Kuplevakhskii & Fal'ko [33]. In turn, by properly adjusting the exchange splitting the position of the Andreev bound states can be moved to the Fermi energy. The system under such circumstances behaves like that being in the π-junction phase as the spontaneous current is generated [34]. However the physical origin of these states is quite different.

In the present paper the properties of the FM/SC heterostructures are discussed in terms of the $FFLO$ state and Andreev bound states. In some situations the state, which has properties of both the $FFLO$ and the π-junction, is realized, leading to various interesting and unexpected phenomena. The present paper is not intending to be a review article, as many issues have been omitted, but a brief look at the results of the recent experiments on FM/SC heterostructures from point of view of the $FFLO$ - Andreev bound states physics.

The paper is organized as follows: In the Section 2 some notable experimental results are presented. Sections 3 and 4 refer to the Fulde - Ferrell - Larkin - Ovchinnikov state in the exchange split bulk superconductor and FM/SC heterostructure respectively. The origin and the nature of the Andreev bound states is explained in Sec. 5, while their realization in FM/SC is studied in Sec. 6. Some recent results regarding the generation of the spontaneous currents in those systems are presented in Sec. 7 and finally, Sec. 8 contains summary and some concluding remarks.

2 Surprising experimental results

Since pioneering experiments on spin polarized tunneling in superconductors [35] a large experimental and theoretical effort has been done to understand the interplay between ferromagnetism and superconductivity in the FM/SC hybrid structures. According to the conventional point of view the proximity effect in FM/SC system should be very short ranged due to the destructive nature of the ferromagnetism on superconductivity. However some of the experiments seem to be in contradiction to this conventional wisdom.

2.1 Conductance and magnetoconductance

Lawrence and Giordano [36] measured the magnetoresistance of $Pb/Ni/Pb$ and $In/Ni/In$ structures and found it to be two orders of magnitude larger than it was predicted by theory. The effect has been attributed to an 'unusual' proximity behavior. Petrashov *et al.* [37] studied the proximity-induced conductance on the FM side of the hybrid FM/SC (Ni/Al) structures and again difference between experiment and theory was two orders of magnitude. Moreover they have observed new peaks in the differential conductance on the superconducting side, giving a clear evidence of a strong mutual proximity effect. Very long range proximity effect with new peaks in magnetoresistance of the ferromagnetic (Ni) wires deposited on SC (Al) have also been observed and explained analyzing the topologies of actual Fermi surfaces in ferromagnet [38]. Another experiment on Co/Al nanostructure [39] showed a drop in resistance of the Co wire, while differential conductance data suggested decay length for proximity effect to be about 180 nm, which is an order of the magnitude larger than that expected from the exchange field of the ferromagnet. Similar conclusions have been reached by Petrashov *et al.* [8] in the case of SC (Al) islands deposited on FM (Ni) structure. All above transport experiments support the very long range proximity effect scenario in such FM/SC heterostructures. However, there are also alternative explanations due to the spin accumulation effect at the FM/SC interface [40] or anisotropic magnetoresistance [41].

2.2 Interface properties

The important problem in the transport experiments is the quality of the interface. The issue has been raised by Aarts *et al.* [42] suggesting that interface transparency for the Cooper pairs strongly depends on the pair breaking effect in FM layer and hence on the exchange field. Indeed it has been shown theoretically [43] that interface resistance can, not only quantitatively but also qualitatively, modified transport properties of the FM/SC heterostructures consisted of either BCS or high-T_c superconductors. For the $Nb/Al/Gd/Al/Nb$ junction it has been confirmed experimentally that main contribution to the resistance comes from the interface scattering (unlike the NM/SC case, where the bulk scattering is very important) by Bourgeois *et al.* [44]. Moreover, the explanation of the measured conductance of the Co/Pb nanocontacts by Soulen *et al.* [15], needs some modifications of properties of the interface even though a band structure of the materials is taken into account [45].

2.3 Transition temperature - FM/SC multilayers

Since it is easy to measure, most of the experimental efforts has focused on the SC transition temperature of the FM/SC multilayers, sometimes showing surprising and intriguing results. Wong *et al.* [24] for the first time has observed oscillations of the SC transition temperature T_c as a function of the FM slab thickness in Fe/V multilayers. The result remained in a contradiction with the conventional point of view of the destructive nature of the ferromagnetism on superconductivity. This curious behavior has been attributed to the formation of an effective π-junction in such structure [21]. At certain thicknesses of the FM layer the state with the phase of the order parameter across the FM layer equal to π is realized rather than usual 0 state. So when the thickness of the FM is varied, the system chooses the state with the higher T_c, thus switching between 0 and π-phase.

The oscillations of T_c have also been seen in structures consisted of other materials, usually metallic ferromagnets and superconductors like Gd/Nb [46], Co/Nb and Co/V [47]. The oscillating behavior also have been found in $CuMn/Nb$ (spin-glass/superconductor) multilayers [48] and even in an insulating ferromagnet/superconductor (GdN/NbN) system [49]. The example of such behavior of the T_c as a function of the FM thickness d_{Gd} is shown in the Fig. 1, taken from Ref. [46]. The system consisted of Gd/Nb multilayers sputtered on Si substrate. The

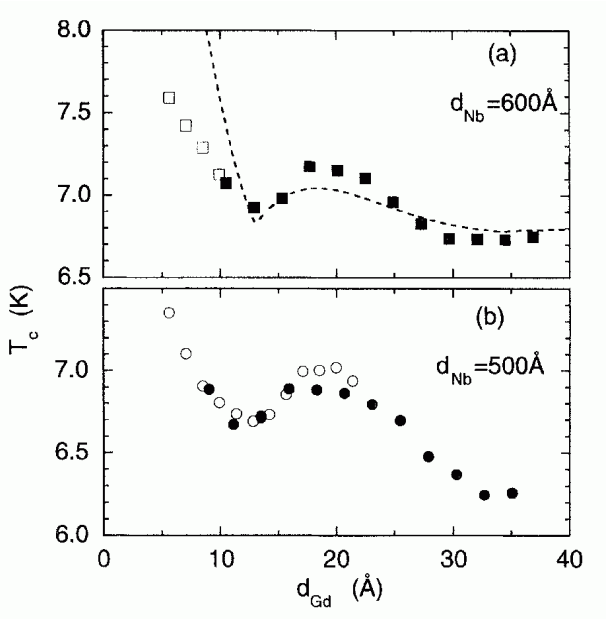

Figure 1: Superconducting transition temperature T_c vs FM thickness d_{Gd} in Gd/Nb multilayers with (a) $d_{Nb} = 600$ $\AA$ and (b) 500 $\AA$. Different symbols correspond to different sample series. Data reproduced from Ref. [46].

critical temperature has been determined from resistivity measurements by standard four-probe technique as well as from ac susceptibility.

Subsequent experiments [50]-[52] have shown no oscillations of T_c. In particular, Koorewaar *et al.* [50] studied T_c in Fe/V multilayers and concluded that superconductivity is decoupled even

by ultrathin Fe layers. Strunk *et al.* explained monotonic behavior of T_c by short penetration depth of the Cooper pairs in Gd/Nb system. No oscillations have been observed in VFe/V multilayers [42] due to the interface scattering. Verbanck *et al.* [52] observed also monotonic behavior of T_c, however at certain value of the Fe thickness of the Fe/Nb system T_c vs d_{Fe} curve showed sudden drop. This effect is due to the non-magnetic behavior of thin Fe slab, while for larger Fe thicknesses the Nb layers are decoupled by Fe which became ferromagnetic.

In fact one can explain both behaviors: the oscillations of T_c and their lack by including spin-orbit coupling into theory [53]. While the exchange filed in FM is responsible for oscillations, the spin-orbit coupling tends to suppress them. So in general the π-junction scenario [20, 21, 54] has been wide accepted as an explanation of the oscillatory behavior of the superconducting transition temperature in FM/SC multilayers.

2.4 Transition temperature - FM/SC/FM trilayers

Some of the experiments performed on $FM/SC/FM$ trilayers [55]-[57] and even FM/SC bilayers [57] showed also oscillating nature of T_c. Such curious behavior cannot be explained with help of the π-junction, because simply there is only one SC layer. So other explanations have been proposed. Mühge *et al.* [55] studied $Fe/Nb/Fe$ trilayer and the observed oscillations of T_c explained in terms of a rather complex behavior of the magnetically "dead" Fe layer near the interface. They argued that at low d_{Fe} the layer is a strong pair breaker due to induction of the repulsive electron-electron interaction by Fe d-levels. Further, at certain d_{Fe} T_c start to raise because the FM order in Fe is nucleated leading to a Zeeman splitting of the d-states and reducing the repulsive interaction. And finally, the maximum and further decrease of T_c occur due to the domination of the direct exchange splitting as the thickness increases. Tagirov *et al.* [56] observed not only oscillations of T_c but also re-entrant effect in $Fe/V/Fe$ trilayers. At certain d_{Fe} the superconductivity is destroyed, and as the FM thickness is increased further, the SC state is recovered. The other experiments showed non-monotonic behavior of T_c in $Fe/Pb/Fe$ [57] trilayers and even bilayers: Fe/Pb [57] and $CuNi/Nb$ [58]. Certainly such behavior is a clear indication of an unconventional, propagating state in the ferromagnet in proximity to the superconductor. Finally, there were other works on similar structures where the oscillations have not been found [59]. Also result was negative for $Fe/Pt/Nb$ ($FM/NM/SC$) trilayers [60] due to the strong influence of the non-magnetic (Pt) spacer.

Subsequent theoretical works [22, 23, 61]-[64] showed that oscillations of the superconducting transition temperature could be also explained in terms of the Fulde - Ferrell - Larkin - Ovchinnikov ($FFLO$) state [18, 19]. Moreover, the $FFLO$ scenario allows for a non-monotonic behavior of T_c even for bilayers [22, 23, 56]-[63]. So this makes the $FFLO$ scenario a natural explanation of the oscillatory behavior of T_c in the FM/SC heterostructures. The fact that in some experiments oscillations of T_c have been seen [24, 46]-[49, 55]-[57] and in other have not [50]-[52, 59, 60] can be due to the properties of the FM/SC interfaces (transparency) [23, 63] as well as due to the disorder [22, 23, 62]. Such scenario is consistent with the recent experiment [65], where T_c in $Nb/PdFe/Nb$ has been studied, and the T_c showed its oscillatory behavior or did not, depending on the iron concentration. However the results cannot rule out the π-junction behavior, as there are two SC layers in this system.

There is another aspect supporting the realization of the $FFLO$ state in FM/SC structures. Despite the oscillations of the T_c, sometimes the sudden kink at certain value of the FM thickness was observed [66, 56]. This effect cannot be explained neither in terms of the π-junction behavior nor by usual $FFLO$ state, in which the pairing amplitude varies only in the direction perpendicular to the interface. However it turns out that at certain conditions $3D$-$FFLO$ state, featuring in spatial dependence of the pairing amplitude also along the interface, can be realized [67, 6]. In this case the system chooses the lower energy ground state and is switched between usual $1D$ and $3D$ $FFLO$ state producing sudden jump of the critical temperature. Of course, the oscillations of T_c, their lack and reentrance of the SC can be also realized within this scenario.

Recently it has been predicted theoretically [13, 20, 62, 63] that the $FM/SC/FM$ systems should exhibit different SC transition temperatures depending on the direction of the magnetization in the FM layers. In particular it can be switched between superconducting and normal states in antiparallel and parallel magnetization configurations respectively. This effect has been observed experimentally [69].

2.5 Critical Josephson current

The question of the π-junction behavior has been also addressed theoretically, studying the Josephson critical current through ferromagnetic spacer [20, 70]-[76]. It has been predicted [20], that Josephson critical current I_c should exhibit an anomalous FM thickness dependence while switching between 0 and π-phase. In particular the amplitude of I_c should go to zero at the transition point ($d_{FM} = d_{FM}^{crit}$). Similar behavior is expected for the system with properly adjusted FM thickness ($d_{FM} = d_{FM}^{crit}$) when the temperature is changed (see however [76]). First experimental evidence of the π-junction has been given by Ryazanov *et al.* [77], where the critical Josephson current in the $Nb/CuNi/Nb$ trilayer has been measured as a function of the temperature (see Fig. 2). They found that I_c vanishes at the transition point. In fact I_c does not have to be zero, at this point due to the higher order Josephson coupling [76]. Another experiment [78], measuring I_c in $Nb/Al/Al0/PdNi/Nb$, but as a function of the FM layer thickness, also confirmed realization of the π-junction state in this system.

2.6 Tunneling and the density of states

One of the features of the π-junction state is the zero-bias conductance peak ($ZBCP$) [29]. In fact such $ZBCP$ has been observed very recently in $Nb/FeSi/Nb$ tunnel junction [79]. Interestingly, it turns out that, due to the polarization of FM and the Fermi wave vector mismatch between FM and SC regions, the $ZBCP$ can also emerge when the conductance of the FM/SC bilayer is calculated [43]. However, in Ref. [43] a step like function for the pairing potential $\Delta(\mathbf{r})$ has been assumed, thus neglecting the proximity effect. If $\Delta(\mathbf{r})$ is calculated self-consistently, we believe that $ZBCP$ can also emerge without the Fermi wave vector mismatch due to the $FFLO$ Andreev bound states in the system [80, 81].

The density of states (DOS) at the Fermi energy shows the oscillatory behavior as a function of the thickness of the FM layer [82]-[85, 34, 80, 81]. The oscillations of DOS have been

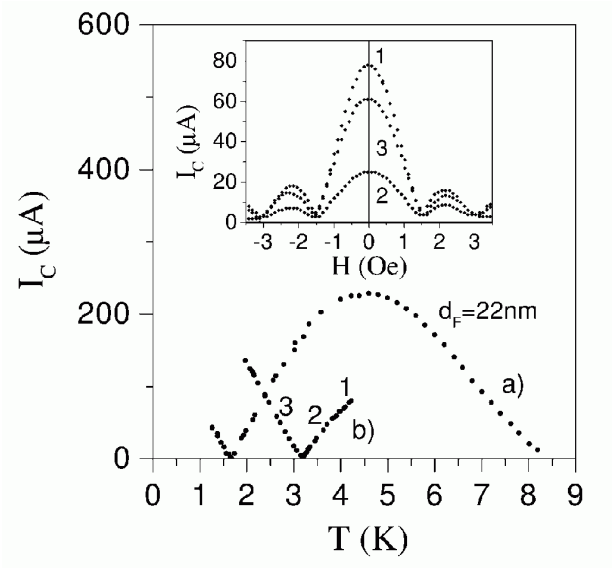

Figure 2: Critical current I_c in the $Nb/CuNi/Nb$ heterostructure as a function of temperature T for two junctions with $Cu_{0.48}Ni_{0.52}$ and $d_{FM} = 22\ nm$. Inset: I_c versus magnetic field H for the temperatures around the crossover to the π state as indicated on curve b): 1 - $T = 4.19\ K$, 2 - 3.45 K and 3 - 2.61 K. Data reproduced from Ref. [77].

observed experimentally [25] in the planar tunneling spectroscopy of the $Al/AlO/PdNi/Nb$ heterostructure. The results are depicted in the Fig. 3. The experimental results have been quantitatively explained in terms of the $FFLO$ scenario and Andreev bound states [83, 82, 86]. However, additionally the effect of the finite interface resistance had to be taken into account [25, 83, 82, 86] in order to get the quantitative agreement with experiment [25]. On the other hand, the disorder due to the impurity scattering is of no importance in this system as the good fit has been achieved in the clean limit.

The other experiments regarding magnetic proximity effect [87], magnetic coupling through the SC spacer [88, 89] and experiments on colossal magnetoresistance materials in contact with high-T_c superconductors [10] have been omitted. The only those important from a point of view of the present paper, $FFLO$ Andreev bound states physics, have been discussed.

3 Superconducting electrons in an exchange field - FFLO state

It is well known that the exchange field tends to polarize the conduction electrons in a metal. Now the question raises what will happen if these electrons are Cooper paired. In other words what will be effect of the exchange field on superconductor. At zero temperature, naively one would expect that this field is either too weak to break the Cooper pairs, thus it leaves the SC state unchanged, or it produces a first order phase transition to the normal state. However, it turns out that for certain values of the exchange splitting a new supercondcuting depairing ground state, with both the Cooper pairs and unpaired electrons present, can be realized [18, 19]. This state is known as *Fulde - Ferrell - Larkin - Ovchinnikov* ($FFLO$) state and it evolves from

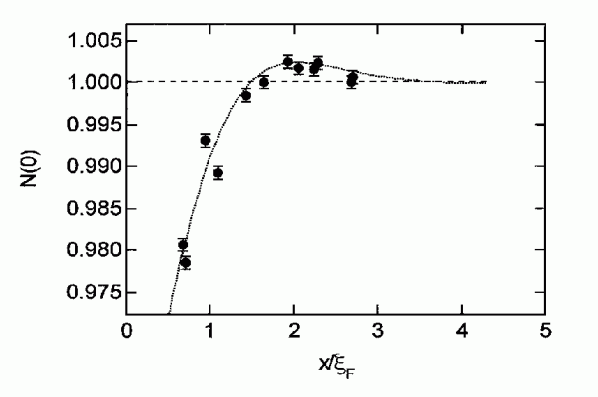

Figure 3: Tunneling conductance of the $Al/AlO/PdNi/Nb$ junction at zero energy vs the $PdNi$ thickness normalized by the coherence length ξ_{FM}. The data taken at $T = 300\ mK$ and $H = 100\ G$ are shown as solid symbols. The dotted line represents theoretical fit, while the dashed one denotes the transition from the 0- to the π-state. From [25].

the BCS, by the first order, to the normal state, by the second order phase transition, as the exchange energy is increased. Actually this is true only for the $3D$ superconductor with the spherical Fermi surface, as it was shown later [90] the phase diagram of such system strongly depends on dimensionality and thus properties of the Fermi surface. The phase diagram of the $3D$ BCS superconductor in an exchange field is shown in the Fig. 4. One can note that $FFLO$

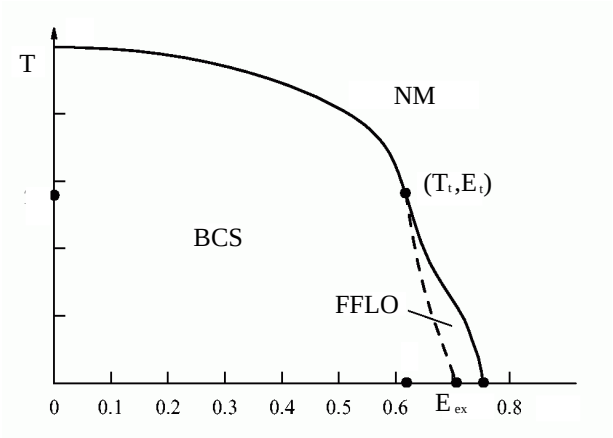

Figure 4: (T, E_{ex}) phase diagram of the BCS superconductor in the exchange field. E_{ex} is in units of Δ_0. (T_t, E_t) denotes tricritical point with $T_t = 0.56T_c$ and $E_t \approx 0.62\Delta_0$. Solid line denotes second order phase transition and the dashed one - first order. Reproduced form [6].

state is realized only in very narrow range of parameters.

The $FFLO$ state is characterized by spatially dependent order parameter corresponding to the non-zero center of mass motion of the Cooper pairs, i. e. $\Delta(\mathbf{r}) = \Delta_0 e^{i\mathbf{Qr}}$ [18] or $\Delta(\mathbf{r}) = \Delta_0 cos(\mathbf{Qr})$ [19] with $\mathbf{Q}$ depending on the exchange splitting E_{ex} and the Fermi velocity v_F ($|\mathbf{Q}| = 2E_{ex}/v_F$). At this point it well to raise an issue regarding the physical origin of such

oscillations. Imagine a Cooper pair subjected to the exchange field E_{ex}. Upon acting of E_{ex} the pair is not an eigenstate any more. Moreover, due to the exchange field, the spin up electron in the Cooper pair lowers its potential energy, while the spin down electron raises it. On the other hand, the total energy has to be conserved for each electron, so the spin up (down) electron must increase (decrease) its kinetic energy (see upper part of Fig. 5). And thus the Cooper pair

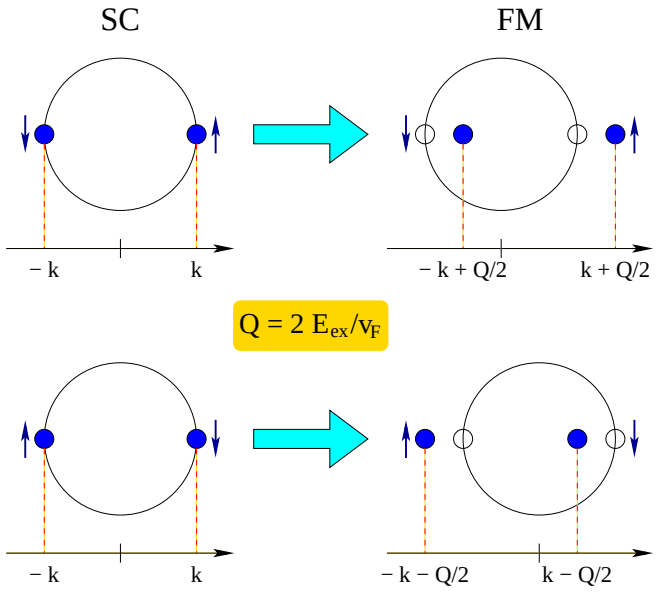

Figure 5: Cooper pairs in superconductor (SC) and in superconductor in an exchange field (FM). Adapted from Ref. [22].

acquires a center of mass momentum **Q**. Similar is true for the pair with its spins interchanged, shown on the bottom of Fig. 5.

The $FFLO$ state has some polarization due to the unpaired electrons and hence it displays almost normal Sommerfeld specific heat and single electron tunneling characteristics [18, 91]. The non-zero value of pairing **Q** also gives rise to the unusual anisotropic electrodynamic properties [18, 91]. Another feature of this state is a current flow in the ground state. It consists of two parts. One is due to the unpaired electrons, which tend to congregate at one portion of the Fermi surface, and the other one is a supercurrent generated by the non-zero value of the pairing momentum. Both currents flow in opposite directions, thus cancel each out, so the Bloch theorem (no current in the ground state) is satisfied. Finally, it turns out that this state is very sensitive to both potential scattering τ_f and spin-orbit scattering τ_{so} and is destroyed when the product of the mean free time and BSC energy gap Δ_0 is equal to unity [91]. This may be the reason why there is no unambiguous experimental evidence of the $FFLO$ state in bulk materials. However this state might already be seen in some quasi-two-dimensional organic conductors (see e.g. [92]).

4 FFLO state in FM/SC heterostructures

It is widely accepted that $FFLO$ state in natural way can emerge in the ferromagnet/superconductor heterostructures. One can imagine that the Cooper pair from SC enters into FM and experiences the exchange field [22]. In this case, the pair is not a eigenstate of FM, so it becomes an evanescent state, exponentially decaying over the distance of the normal metal coherence length, as in the case of usual proximity effect [4]. Moreover, due to the exchange splitting, it acquires a center of mass momentum $\mathbf{Q}$. So the wave function of the pair (or pairing amplitude $\chi(\mathbf{r})$) receives a spatial modulation, similarly as in the bulk SC pairing potential $\Delta(\mathbf{r})$ does [93]. In general, one has to take into account both cases, shown in the upper and lower parts of the Fig. 5. According to this picture, the 'upper' Cooper pair wave function acquires the momentum equal to $\mathbf{Q}$, while the 'lower' one $-\mathbf{Q}$, so the modulation factor is $cos(\mathbf{Qr})$, like for the scenario proposed in Ref. [19]. This is true for the Cooper pair moving perpendicular to the FM/SC interface. Now if one assumes all possible angles of incidence for this pair, the spatial modulation of the pairing amplitude in FM is given by $sin(x/\xi_{FM})/(x/\xi_{FM})$ [22], where x is the distance from the interface, while $\xi_{FM} = \hbar v_{FM}/E_{ex}$ is the FM coherence length. Typical example of such behavior, obtained numerically [80], is shown in the Fig. 6. It turns out that, unlike in the

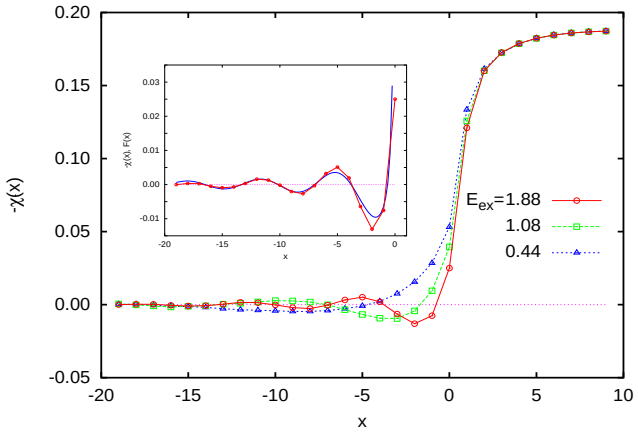

Figure 6: The pairing amplitude vs distance from the interface x for values of the exchange field indicated in the figure, in units of $t = W/8$, where W is a bandwidth. Inset: comparison of the numerical results with the analytical formula $\chi(x) \propto sin(x/\xi_{FM})/(x/\xi_{FM})$ for the exchange field $E_{ex} = 1.88$. From Ref. [80].

bulk SC, these oscillations are obtained for a wide range of the parameters [22, 94, 84, 34, 80], so it means that $FFLO$ state can be more easily realized in FM/SC heterostructures. Indeed, such oscillations have been indirectly seen experimentally by Kontos *et al.* [25]. Similar oscillations have also been predicted [95, 96] for a superconductor with d-wave symmetry of the order parameter. Additionally it has been observed to be generating a p-wave component of the SC order parameter near the interface [95].

The important issue is the question of disorder, as it is known to be very destructive for the bulk $FFLO$ state [91]. Namely, the $FFLO$ phase disappears when $1/\tau_f$ or $1/\tau_{so} > \Delta_0$. The situation is quite different in FM/SC proximity system, where superconductivity and magnetism

are spatially separated. Of course, the effect of both the elastic potential and the spin-orbit scattering is to lower the effective period of the oscillations of the pairing amplitude as well as to introduce additional its decay [22]. In particular, in the dirty limit (strong disorder), the oscillations are damped on the same length scale on which they oscillate, so the $FFLO$ state is suppressed. However, the mean free time (between successive scattering events) is proportional to $1/E_{ex}$ rather than $1/\Delta_0$, as the energy scale in ferromagnet is set by the exchange splitting only (the SC gap parameter Δ_0 vanishes in FM). So one can say that the disorder is less destructive for the $FFLO$ state in this case. Moreover, the stronger ferromagnet is, the larger disorder is required to destroy the $FFLO$ state. This is the reason why the $FFLO$ state has been observed experimentally in FM/SC heterostructures even the ferromagnet was an alloy, like in [58, 65, 25].

By taking into account the effect of the elastic scattering (non-magnetic disorder) in the $FFLO$ state, one can theoretically describe all behaviors of SC transition temperature T_c observed experimentally: oscillations of T_c or their lack as well as the reentrant superconductivity. The example of such behavior for FM/SC bilayer is shown in the Fig. 7, taken from Ref. [23]. However, for a complete calculations the requirement of a finite interface transparency has also

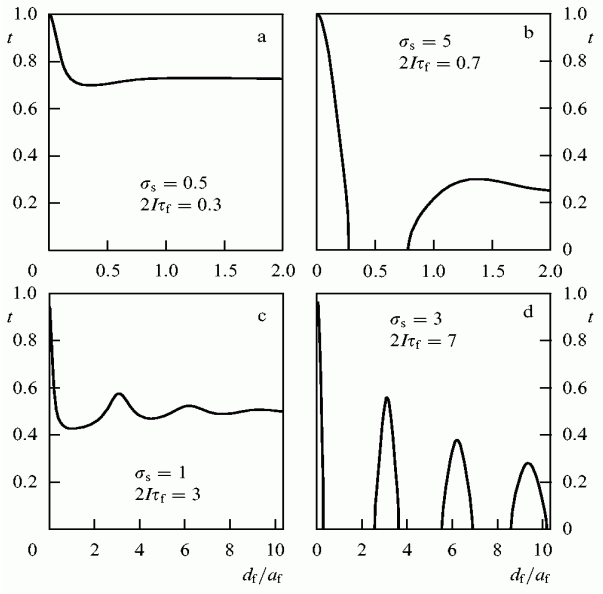

Figure 7: Reduced transition temperature $t = T_c/T_{BCS}$ as a function of the reduced thickness of the FM layer for different strengths of disorder τ_f (from a) strongest disorder to d) cleanest system). σ_S is the interface transmittance and $I \equiv E_{ex}$. Plot a) represents emergence of T_c onto a plateau; b) reentrant superconductivity; c) oscillations of T_c; d) periodically reentrant superconductivity. The dashed curves t^* in parts b and d represent lines of tricritical points. Adapted from Ref. [23].

to be assumed.

As it was mentioned, the bulk $FFLO$ state also features spontaneously generated currents, flowing in the ground state. Similar currents have been recently predicted [34, 80, 81] to occur in FM/SC proximity effect. Such currents flow, depending on the exchange splitting and the

thickness of FM layer. The origin of these currents and the conditions for their flowing are closely related to the Andreev bound states in FM/SC heterostructures [34, 80, 81] and will be discussed in Sec. 7.

5 Origin of Andreev bound states

From quasiclassical considerations, each bound state corresponds to particle moving along a family of closed trajectories [97]. The energy of such bound state is determined by the Bohr-Sommerfeld quantization rules, according to which the total phase accumulated during one cycle has to be equal to multiples of 2π. Interestingly, the bound states also emerge in the normal metal/superconductor (NM/SC) structures [31] due to the Andreev reflections [3], according to which an incident electron is reflected back as a hole at the interface, and a Cooper pair is created in SC. Such states are built up from a combination of electron and hole wave functions. The example of the closed quasiparticle trajectory, producing the bound state, in an insulator/(normal metal)/superconductor $I/NM/SC$, is shown in the Fig. 8. It consists of an

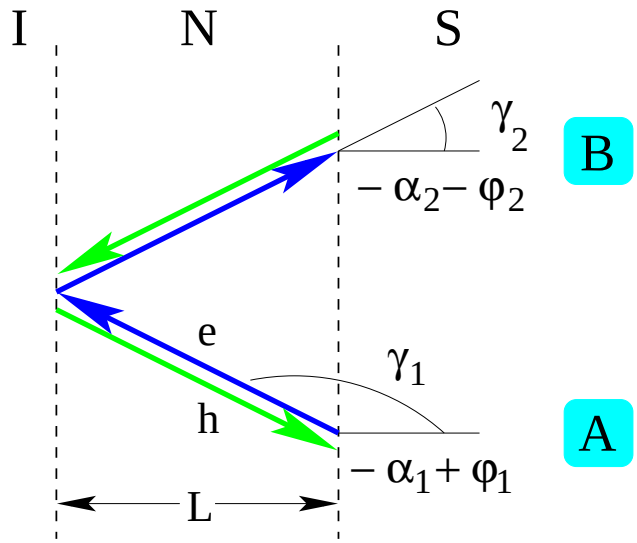

Figure 8: The example of the quasiparticle path corresponding to the Andreev reflections, giving a bound state. The quasiparticle is trapped in the normal region because of normal reflection at the I/NM surface and the Andreev reflection at the NM/SC interface. The total phase accumulated during one cycle is equal: $-(\alpha_1+\alpha_2)\pm(\varphi_1-\varphi_2)+\beta(E)$.

electron e segment, which includes a ordinary reflection at the I/NM interface, and hole h one, retracing backwards the electron trajectory. The total accumulated phase in this case consists of contribution from Andreev reflections at point A: $-\alpha_1+\varphi_1$ and B: $-\alpha_2+\varphi_2$ as well as contribution from the propagation through the normal metal $\beta(E)$. $\alpha_{1(2)}=arccos(E/|\Delta_0|)$ is the Andreev reflection phase shift, while $\varphi_{1(2)}$ is the phase of the SC order parameter at point A (B). $\beta(E)=2L(k_e-k_h)+\beta_0$ is the electron-hole dephasing factor and describes the phase acquired during the propagation through the normal region, where the first term corresponds to the ballistic motion and the second one to the reflection at the I/NM surface. L is the thickness

of NM, and k_e (k_h) is the electron (hole) wave vector. Thus the Bohr-Sommerfeld quantization condition is:

$$-(\alpha_1 + \alpha_2) \pm (\varphi_1 - \varphi_2) + \beta(E) = 2n\pi \tag{1}$$

where the $\pm(\varphi_1 - \varphi_2)$ stands for the trajectories in the $\pm k_y$ (parallel to the interface) direction.

If there is no phase difference between points A and B in the Fig. 8, as for instance in the case of the (normal metal)/(s-wave superconductor) interface, Eq. (1) gives the energies of the bound states in the form [31]:

$$\frac{E}{\Delta_0} = \pm cos\left(\frac{2EL}{\Delta_0 \xi_0 cos(\gamma_2)}\right) \tag{2}$$

where $\xi_0 = \hbar v_F/\Delta_0$ is the SC coherence length and γ_2 is the angle between electron trajectory and the surface normal (see Fig. 8). The number of such states for each quasiparticle trajectory is determined by the length of the quasiparticle path, which in turn is given by the NM thickness and the propagation angle γ_2.

As it can be read from Eq. (2), the bound states always appear in pairs symmetrically positioned around the Fermi level because of the time reversal symmetry in the problem. Moreover, due to the fact that there is no difference between electrons and holes at the Fermi level ($\beta(E = 0) = 0$), there is no $E = 0$ solution. In other words, the bound states always emerge at finite energies.

The situation is quite different if there is a phase difference $(\varphi_1 - \varphi_2)$ between points A and B (see Fig. 8). The example can be the interfaces with d-wave superconductors oriented in the (110) direction, where $(\varphi_1 - \varphi_2) = \pi$. In this case, due to the additional phase shift π, the Eq. (1) has the solution:

$$\frac{E}{|\Delta_0|} = \pm sin\left(\frac{2EL}{|\Delta_0| \xi_0 cos(\gamma_2)}\right) \tag{3}$$

From this it follows that bound states can emerge even at zero energy. Such zero-energy Andreev bound states, in the case of high-T_c superconductors, have been predicted by Hu [32] and are known as *zero-energy mid-gap states*. The presence of the Andreev bound states at zero energy features in many important effects, like zero-bias conductance peaks, π-junction behavior, anomalous temperature dependence of the critical Josephson current, paramagnetic Meissner effect, time reversal symmetry breaking and spontaneous interface currents [29, 30].

Although the zero-energy states (ZES) are likely to appear when the phase of the order parameter at the interface is not constant, the resulting density of states at the Fermi energy is energetically unfavorable and any mechanism able to split these states will lower the energy of the system [30, 98]. On of these is the self-induced Doppler shift [99, 29] $\delta = ev_F A$, where A is a vector potential. The situation is schematically depicted in the Fig. 9. At low temperature ($T^* \approx (\xi_0/\lambda)T_c$, where λ is the penetration depth of the magnetic field) the splitting of the zero energy states produces a surface current. This current generates a magnetic field (screened by a supercurrent), which further splits ZES due to the Doppler shift effect. The effect saturates when the magnetic energy is equal to the energy of the Doppler shifted ZES.

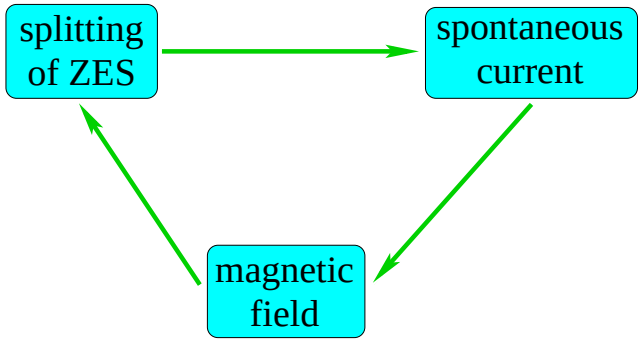

Figure 9: Generating of the spontaneous currents.

6 Andreev bound states in I/FM/SC trilayer

Naturally, the Andreev bound states also arises in $I/FM/SC$ heterostructures [33, 100, 83, 76, 94, 80, 81]. More importantly, as it was first predicted by Kuplevakhskii & Fal'ko [33], it is possible to shift these states to zero energy by tuning the exchange splitting. Again, the energies of such states can be obtained from the quasiclassical arguments (Eq. (1)) with modified electron-hole dephasing factor $\beta(E)$ due to the exchange splitting. Thus the solution of the Eq. (1) now is:

$$\frac{E_\sigma}{\Delta_0} = \pm cos\left(\frac{1}{2} + cos(\varphi_1 - \varphi_2) + \frac{\sigma\pi L}{2cos(\gamma_2)\xi_{FM}}\right) \tag{4}$$

Clearly, the crossing of the zero energy solution can be obtained either by changing the phase difference $(\varphi_1 - \varphi_2)$ or by varying FM coherence length (exchange field). The energies of the bound states as a function of the reduced FM thickness L/ξ_{FM} is shown in the Fig. 10. It is

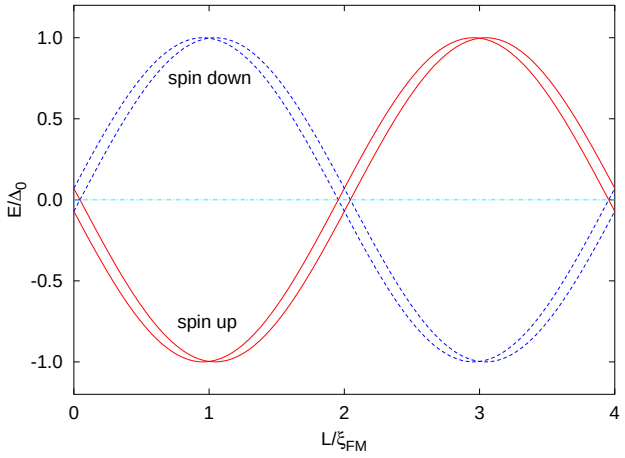

Figure 10: Positions of the Andreev bound states E/Δ_0 as a function of the reduced FM thickness L/ξ_{FM} for $\gamma_2 = 0$ and $(\varphi_1 - \varphi_2) = 0$ (see Fig. 8). The energies obtained from Eq. (4).

worthwhile to note that crossing the zero energy appears periodically, and also depends on the angle of the particle incidence γ_2 (see Fig. 8).

The properties of such bound states have been also studied fully quantum-mechanically within lattice models of the FM/SC systems [94, 80, 81] and similar their behavior have been obtained. Interestingly, it turns out, that as in the case of the high-T_c structures [99], such zero energy Andreev states support spontaneous currents flowing in the ground state of the FM/SC system [34, 80, 81]. The mechanism of generating of such currents is the same, as earlier discussed, namely the self-induced Doppler shift. So in fact, when the current flows, such one of the states will be twice shifted: once due to the exchange (Zeeman) splitting, and the second time due to the Doppler shift. Schematically, the situation is depicted in the Fig. 11.

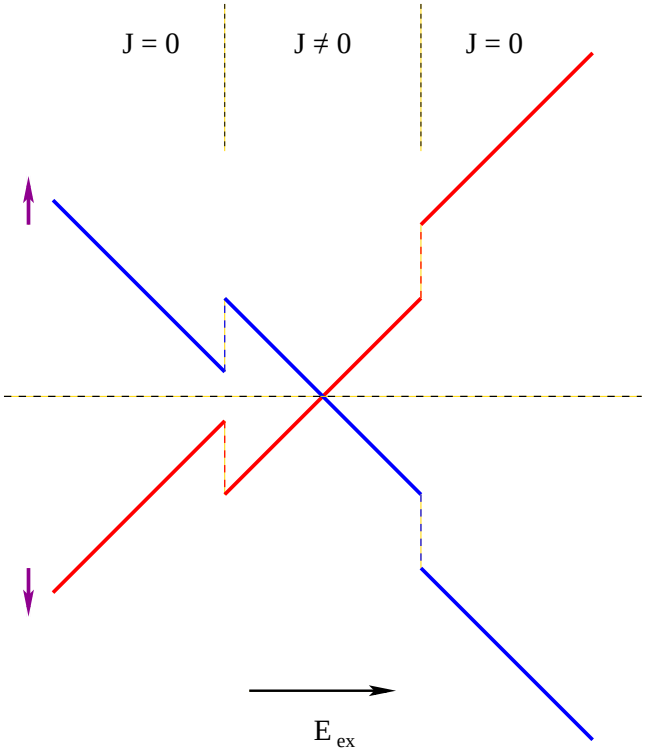

Figure 11: The effect of the spontaneous current on the positions of Andreev bound states. Despite usual (Zeeman) splitting ($J = 0$), there is also Doppler shift due to the current flowing ($J \neq 0$).

For energies less than superconducting gap, the only Andreev bound states will contribute to the density of states $\rho(E)$. However, as it was mentioned, for fixed thickness and exchange splitting, there will be Andreev bound states at different energies, for different angles of particle incidence (γ_2 in the Fig. 8). Thus to get the density of states, one has to sum the energies of these states over all values of γ_2:

$$\rho(E) = \sum_{\gamma_2=-\pi/2}^{\pi/2} \delta(E - E_{bound}) \tag{5}$$

and talk, in fact, about Andreev bands rather that single states. However, all that was said on properties of the bound states, remains true for Andreev bands too. In particular the splitting of the whole band due to the spontaneous current is ilustrated in the Fig. 12. The additional structure comes from the other (higher order) Andreev reflections. Superconducting energy gap $\Delta_0 = 0.376$ in this figure.

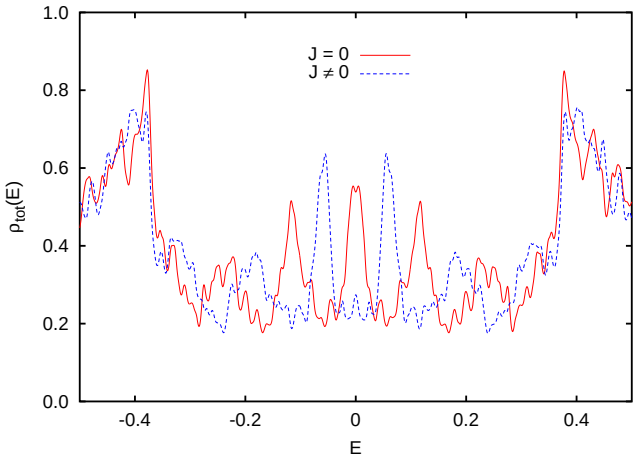

Figure 12: Doppler splitting of the zero-energy state. From Ref. [80].

There is also a strong correlation between Andreev bound states (bands) and the pairing amplitude [94, 34, 80]. Each time the pairing amplitude at the I/FM interface changes its sign, the Andreev bound state (band) crosses the Fermi energy. Moreover in this case the spontaneous current is generated.

7 Spontaneous currents

One of the most remarkable properties of the ferromagnet/superconductor proximity systems is the appearance of spontaneous currents flowing in the ground state. Such currents have been recently predicted [34, 80, 81] in fully self-consistent treatment of the $I/FM/SC$ trilayers within a simple tight binding Hubbard model. These currents appear even there is no any external magnetic filed and, as it could be expected, in the case of ferromagnet, they are spin-polarized under certain conditions.

7.1 Linear current response

As it was mentioned, the large density of states at the Fermi level is energetically unfavorable, so the spontaneous current is generated thus lowering the energy of the system. The appearance of the spontaneous currents can be explained very easily within linear current response theory [101]. According to this the total current can be divided into two parts: diamagnetic one giving a response of the bulk density and the paramagnetic one, which is due to the deformation of the wave function at the Fermi surface and thus proportional to the density of states at the Fermi level (at $T = 0$). So if $\rho(E_F) = 0$, the paramagnetic current vanishes, and nothing is happening when there is no external magnetic field. On the other hand, if there is a sharp peak at E_F, this gives rise to the paramagnetic current, which overcompensates the diamagnetic one and thus leads to the instability and creation of the spontaneous current. So in fact one can say that spontaneous current is proportional to the density of states at the Fermi level.

7.2 Fully self-consistent treatment

The spontaneous current appears in a natural way when the FM/SC system is treated self-consistently within the lattice tight bounding Hubbard model [34, 80, 81]. In this case a number of equations for SC order parameter, spin polarization, chemical potential, current and its polarization as well as a vector potential has to be solved fully self-consistently. Details of calculations, which fully confirm the above picture, can be found in [80].

The typical example of such current, flowing parallel to the FM/SC interface, is shown in the Fig. 13. The current flows mostly in positive y direction on ferromagnetic side and in negative

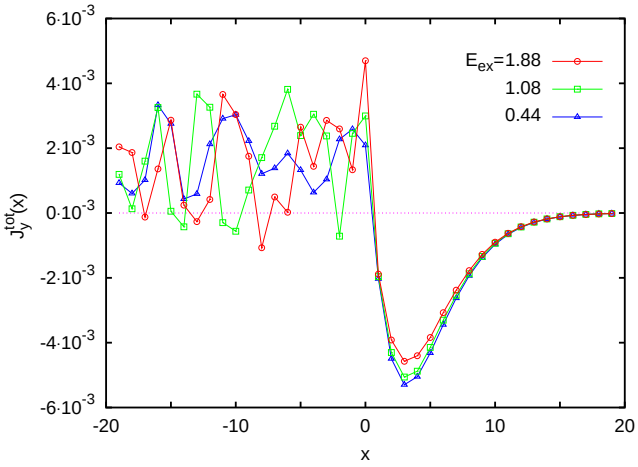

Figure 13: Spontaneous current (in units of $et/\hbar$) flowing parallel to the FM/SC interface for different exchange splittings. From Ref. [80].

direction in superconductor. The total current, integrated over the whole sample, is equal to zero, as it should be for the ground state according to the Bloch theorem. Moreover, the current carrying by quasiparticles exactly cancels the supercurrent [80], as in the bulk $FFLO$ state [18]. In the case of FM/SC system one would expect that supercurrent should flow mainly in superconductor while quasiparticle one in ferromagnet due to the spatial separation of the ferromagnetism and superconductivity. However, it turns out, that this is not the case, one cannot completely spatially separate them. Neveretheless the cancellation does not occur layer by layer and hence locally there are spontaneous currents and magnetic field.

7.3 Spontaneous magnetic field

Obviously, the spontaneous current distribution (see Fig. 13) generates the magnetic field through the sample. The total magnetic flux weakly depends on the thickness of the sample and the exchange splitting. Its magnitude is found to be a fraction of the flux quantum $\Phi_0 = h/2e$ and is smaller than upper critical field of the bulk superconductor. This is rather a large field and could be observable.

Such magnetic field can be used to detect the spontaneous currents. In particular its temperature dependence [81], shown in the Fig. 14. It is worthwhile to note that spontaneous magnetic flux appears below SC transition temperature T_c, at $T^* \approx (\xi_0/\lambda)T_c$. The fact that T^* and T_c are

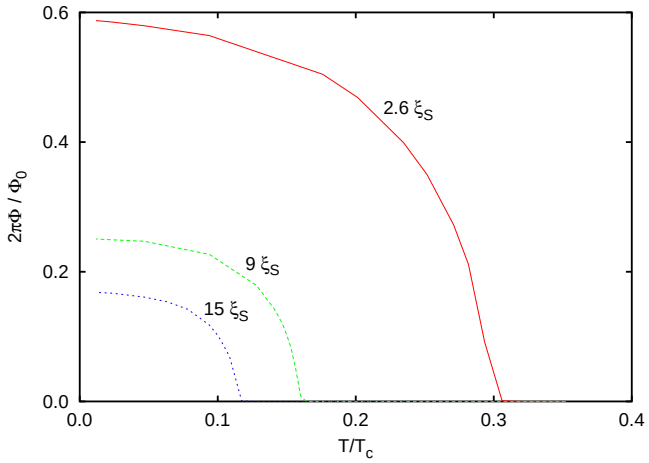

Figure 14: The temperature dependence of the total magnetic flux for different thicknesses of the FM region. From Ref. [81].

different temperatures may help to unambiguously confirm the existence of the spontaneous currents in FM/SC heterostructures.

7.4 Current modified density of states

Owing to the fact that spontaneous currents flow in whole ferromagnet, the splitting of the Andreev bands can be seen in the surface (I/FM) density of states [81], which in turn can be directly measured experimentally [25]. The temperature dependence of the surface density of states at the Fermi energy $\rho(\varepsilon_F)$ (see Fig. 12) can also give a clear indication of such spontaneous current flowing in the system. When the current flows in the system, there is a huge drop in the

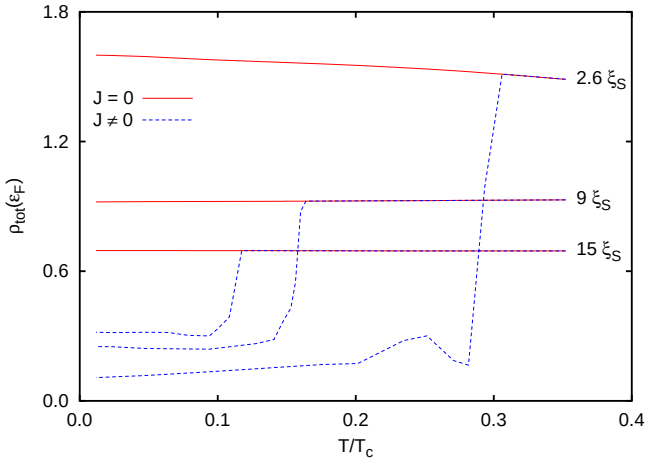

Figure 15: The temperature dependence of the surface I/FM density of states at the Fermi energy. The dashed (solid) line corresponds to the situation in which there is (there is no) current. From Ref. [81].

$\rho(\varepsilon_F)$ at certain temperature $T^* = (\xi_S/\lambda)T_c$, which is usually much smaller that SC transition temperature T_c. Of course such drop in the DOS is caused by the Doppler splitting of the Andreev band.

7.5 Polarization of the current

In the FM/SC proximity system one would expect the spontaneous current to be polarized. It turns out, this is the case only for the ferromagnet with different concentration of electrons and holes, i. e. away from the $e-h$ symmetry point. This can be explained as follows: As it has been discussed at beginning of this section, the spontaneous current is proportional to the density of states at the Fermi energy. In the case of the particle-hole symmetry the density of states for spin up and spin down electrons are the same, regardless the exchange splitting. So as there are no differences in the spin up and spin down DOS, there will not be polarization of the current [34, 80]. Of course in reality, there is no $e-h$ symmetry in ferromagnet, so one would expect non-zero polarization of the current.

7.6 2D FFLO state

As it was mentioned earlier, at certain conditions a $3D$-$FFLO$ state is energetically more favorable than usual $1D$ state. Furthemore, changing the thickness of the FM slab, one can switch the ground state of the system between $3D$ and $1D$-$FFLO$ state [67, 6]. From above self-consistent calculations one can conclude that the same effect emerges in natural way if one considers the spontaneous current in the system. The argument is as follows: The oscillations of the pairing amplitude in the direction perpendicular to the interface occur regardless the spontaneous current. The period of them is related to the x-component of the center of mass momentum of the Cooper pair in FM $\mathbf{Q} = (2E_{ex}/v_F)\frac{\mathbf{v}_F}{v_F}$. This can be interpreted as the usual $1D$-$FFLO$ state in confined geometry, refered to in Sec. 4. On the other hand, in $2D$ geometry studied here, when the current flows parallel to the interface, there is a finite vector potential in the y-direction. This can be regarded as a y-component of the $\mathbf{Q}$-vector. So one can say that when the spontaneous current flows, the $2D$-$FFLO$ state is realized. Moreover when the FM thickness is changed the ground state of the system is switched between $2D$- and $1D$-state, which manifests itself in spontaneous current flow or its lack. Clearly this behavior is consistent with the findings of Izyumov *et al.* [67, 6].

8 Conclusions

The competition between ferromagnetism and superconductivity in FM/SC heterostructures give raise to the Fulde - Ferrell - Larkin - Ovchinnikov ($FFLO$) state in these systems. The original bulk $FFLO$ state manifests itself in a spatial oscillations of the SC order parameter as well as in spontaneously generated currents flowing in the ground state of the system. I have argued that a very interesting version of this phenomenon accures in FM/SC proximity systems. In short, due to the proximity effect and the Andreev reflections at the FM/SC interface, the Andreev bound states appear in the quasiparticle spectrum. These states can be shifted to the zero energy by tuning the exchange splitting or the thickness of the ferromagnet, thus they became zero-energy mid-gap states which lead to various interesting effects. It particular, the spontaneous currents can be also related to the zero-energy states, as in the case of high-T_c superconductors. It seems that some combination of both phenomena is realized in a

real systems. The fact that oscillatory behavior of SC order parameter is strongly correlated with the crossing of the Andreev bound states through Fermi energy and the generation of the spontaneous currents further support $FFLO$ - Andreev bound states picture.

There is also a strong experimental evidence that $FFLO$ - Andreev bound states scenario is really realized in FM/SC structures. This includes the SC transition temperature and the oscillations of the density of states as the thickness of the FM slab is changed. The observation of the $FFLO$ state in such systems is probably related, unlike in the bulk, to its non-sensitivity to a disorder, as it has been suggested theoretically. Additionally, the experimental confirmation of the existence of the spontaneous (spin polarized) currents in the ground state will support the $FFLO$ - Andreev bound states scenario in these structures.

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