Ψ_k Newsletter

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

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Contents

1 Editorial

In this *Newsletter* apart from the 'Progress Report for 1999' in the **ESF Section** we have a report with abstracts on the European Research Conference on **”Electronic Structure of Solids and Surfaces: Challenges in predictive description of reaction dynamics and growth properties at surfaces”**. In the same section there is also a report on CECAM Workshop on **”Electronic Excitations”**, which also contains abstracts. As always, we have a number of abstracts in the usual **Abstracts** section. Announcements of available positions are given in the **General Job Announcements** section. Announcements of meetings/workshops are in the **General Workshop/Conference Announcements** section. The scientific highlight is by J.B. Staunton (*University of Warwick*) *et al.* on **”Spin fluctuations in nearly magnetic metals from ab-initio dynamical spin susceptibility calculations”**. Please check the table of content 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 pointers to home pages of some of the members of our electronic structure community. If you maintain a home page on your activities we will be happy to include a pointer from the *Networks'* home page to your home page.

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

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

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

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

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2 General News

2.1 Psi-k 2000 Conference

Schwäbisch Gmünd, 22-26 August, 2000

"Ab initio (from Electronic Structure) Calculations of Complex Processes in Materials"

Suggestions

Presently we are in the process of deciding on the choice of the plenary and invited speakers for the Psi-k 2000 Conference. If you would still like to suggest speakers and symposia titles for consideration, please fill in within a week the suggestion form at: http://psi-k.ac.uk/psi-k2000

Pre-registration

We would like to encourage pre-registration to the Conference if you have an intention to attend. This would give us a rough idea on the expected number of participants. As you probably know, from the above web page, the Conference is organized by two TMR European Networks and one ESF Programme, and some funds will be available to support the attendance of mostly young people. Of course, only the members of the TMR Networks can apply for support from their sources. Similarly, the ESF can only support scientists from the countries participating to the ESF Programme on "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces". In any circumstance, however, only those contributing a talk or a poster can apply for financial support. Additionally, to the above mentioned organizing bodies, there will be available a small amount of money to partially fund about 20 young scientists from Southern-European countries, that do not participate either to the TMR Networks or the ESF Programme.

3 News from the TMR1 Network "Interface Magnetism"

The application from TMR1 for a Research and Training Network (RTN) under the EU's FP5 was successfully evaluated. The topic of this Network is 'Computational Magnetoelectronics'. The aim of this project is to use the power of Density Functional Theory (DFT) to model, understand and predict transport properties of materials and material systems relevant to magnetoelectronics. The scope and content of this Network ranges from the solution of the basic quantum mechanical equations for the ground state of these systems to realistic calculations of the spin-dependent transport properties of industrial prototypes. These problems will be attacked with the same ab-initio approach, the Green's function method, which allows the formulation, in a transparent way, of spin-dependent transport and moreover guarantees high consistency of the calculated results.

The Network has three inherently connected themes: ground state properties of magnetoelectronic materials, probing the electronic and interface structure of magnetoelectronic materials, spin-dependent transport. These themes are organized in 10 collaborative, scientific tasks of Ferromagnet/Semiconductor Interfaces, Ferromagnet/Oxide Interfaces, Ferromagnet/Superconductor Interfaces, Magnetic Nanostructures, Magnetooptics, Magnetic X-ray Scattering, Giant Magnetoresistance, Tunneling Magnetoresistance, Spin Mesoscopics, Experimental Data and Assessment of Applicability. The Network's composition of ten nodes has as distinguishing features: nodes, which comprise all relevant national theoretical activities, in Daresbury (W.M. Temmerman), Juelich (P.H. Dederichs), Halle (P. Bruno), Paris (A. Fert), Vienna (P. Weinberger), Twente (P. Kelly), Uppsala (B. Johansson); the participation of two Central European nodes from Hungary (J. Kollar) and the Czech Republic (I. Turek); an experimental/industrial team member (Thomson) in the French node, and a US (P. Levy) node.

News of this Network, which is due to start on May 1, 2000, will be published regularly in the Psi-k newsletter.

4 News from the TMR2 Network

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

4.1 Reports on Workshops

4.1.1 Publication of the Report on IWOSMA Workshop

International Workshop on
ORBITAL AND SPIN MAGNETISM OF ACTINIDES
Friday 4 and Saturday 5 June 1999
Daresbury Laboratory, Daresbury
Warrington WA4 4AD, United Kingdom
http://srs.dl.ac.uk/msg
Sponsored by:
European Science Foundation (ESF)
Training and Mobility Research (TMR)2 Psi-k Network

Report on the above meeting has been published in:

Synchrotron Radiation News, Vol. 12, No. 5, pages 13 - 16 (1999).

Reprints are available from g.vanderlaan@dl.ac.uk.

5 News from the ESF Programme

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

STRUC-Ψ_k

5.1 Progress Report for 1999

The aim of the Ψ_k-Research Programme of the ESF is to promote the development and application of computational techniques aimed at an improved understanding of the complex atomistic behaviour of solids and surfaces. The impact of this techniques is not restricted to condensed matter theory, surface science and materials science, but is rapidly expanding into chemistry, mineralogy and even biology, the continuously improved efficiency of the computational tools allowing to tackle problems of immediate industrial relevance. The Ψ_k-Research Programme intends to create a scientific network covering all of Europe with connections to groups in the US and in Japan, and with strong links to experimentalists and industry in the expanding range of applications. When the Ψ_k research programme was started in 1998, it was with fifteen participating countries already the largest of all the research networks created by the ESF. In 1999 the network has been further expanded since Spain and the Czech republic decided to participate in the programme. In view of the very active research groups in both Spain (with particularly promising contributions to the development of O(N) techniques) and the Czech Republic (alloy theory), this is certainly a very valuable addition to the Ψ_k community.

The networking activity within the Ψ_k research programme is based on (a) a bimonthly electronic Ψ_k-Newletter, (b) research workshops, (c) hands-on workshops for disseminating computer-codes, (d) collaborative visits and secondments. A list of the research workshops and collaborative visits organized in 1999 is compiled in the appendix, detailed reports on these activities are published in the Ψ_k-Newletter. The range of topics treated in the research workshops and during the collaborative visits demonstrates the widening impact of the methodology being developed within our research programme.

Among the research workshops those on Catalysis from first principles in Magelas (Denmark), the "hands-on" workshop on Total energy and force methods and ab-initio molecular dynamics held in the International Centre for Theoretical Physics in Trieste, and the Progress in Computational Materials Science in Strasbourg deserve special mention. The Catalysis workshop realized the goal formulated last year of organizing a forum where theoreticians, experimentalist and researchers from industry meet for discussions on front-line research in a field of current technological interest. This very successful meeting also demonstrated the widening impact of computational modelling on industrial research. It was decided to continue this series of meetings in the next years, if the Steering Committee approves. The Trieste workshop was the first of the "hands-on" workshops which aim at disseminating the methologies developed by the leading groups within the Ψ_k community, making the most advanced codes available to a wide range of users. The Strasbourg workshop was the first to be organized in cooperation with the European Materials Research Society (E-MRS). The inclusion of a Ψ_k workshop in the largest European meeting on applied materials science certainly enhances the visibility of computational research within a wide community of materials scientists.

The fruitful interaction with the existing TMR-Networks in the Ψ_k community and with the Centre Européen du Calcul Atomique et Moléculaire (CECAM) has been intensified, as demonstrated by the co-organization of the Materials under pressure, Actinide-magnetism, and Catalysis workshops with one of the TMR Networks, and of the Electronic Exitation workshop with CECAM. The Reaction dynamics and growth at surfaces workshop was organized as a special event in the series of the EURESCO "Structure of solids and surfaces" conferences. These cooperations certainly contribute to enhance the impact of the Ψ_k research programme.

A characteristic feature of all workshops was the active participation of experimentalists and the lively confrontation of the newest theoretical and experimental developments.

The program of collaborative visits and secondments could also be expanded compared to 1998. The topics treated in these joint projects cover a wide area and demonstrate the aim of spreading the use of advanced computational technoligies is well being realized. What is perhaps surprising is that the demand for the support of such visits coming from the participating countries in Eastern Europe was comparatively small. Here the Steering Committee must take a new intitiative to spread the knowledge that such possibilities exist.

For the year 2000 a number of proposals for new workshops has already been submitted. These proposals will be discussed during the meeting of the Core Steering Group on October 23 in Paris. In this session the budget for 2000 will be set up.

Jürgen Hafner
(Acting Chairman)

Appendix 1

Research Workshops within the Ψ_k Research Programme in 1998

Workshop (Organizers)	Location (Date)	Co-organized with
Materials under pressure: From ices to metals (W.Temmerman (Ψ_k))	Daresbury Lab. December 17-18,1998	TMR ”Electronic Structure” UK EPSRC-CCP9
Hydrogen in semiconductors (R. Jones (Ψ_k))	U Exeter April 14-17, 1999	UK EPSRC-CCP9
Orbital and spin magnetism of actinides W. Temmerman (Ψ_k), G. van der Laan	Daresbury Lab. June 4-5, 1999	TMR ”Electronic Structure”
Catalysis from first principles (J.N. Norskøv, M. Scheffler, J. Hafner (all Ψ_k))	Magelas, DK May17-19, 1999	TMR ” Electronic Structure”
Progress in Computational Materials Science (H. Dreyssé, L.T. Wille (Ψ_k))	Strasbourg June 1-4, 1999	European Materials Research Society (E-MRS)
Calculation of materials properties using total energy and force methods and ab-initio Molecular dynamics (J. Kohanoff, J. Neugebauer, M. Scheffler (Ψ_k))	ICTP Trieste August 9-19, 1999	TMR ”Electronic Structure”
Computational Materials Science (V. Fiorentini, P. Ruggerone (Ψ_k))	Villasimius (I) September 10-13, 1999	Regione Autonoma Sardegna UNESCO
Challenges in the predictive description of reaction dynamics and growth properties of surfaces (A. Groß, G. Pacchioni and Th. Klüner (Ψ_k))	Lengries (D) September 18-23, 1999	EURESCO ”Structure of Solids and Surfaces”
Calculation of electronic excitations in finite and infinite systems (L. Reining, G. Onida (Ψ_k), A.Rubio)	Lyon Aug. 31 - Sept.3, 1999	CECAM

Appendix 2

Collaborative visits and secondments within the Ψ_k-Programme

Visitor	Host	Research Topic	Days
R. Kucharczyk (U Wroclaw, PL)	J. Pollmann (U Münster, D)	Electronic properties of superlattices	25
C. Filippi (Univ. College Cork, IRL)	M. Scheffler FHI Berlin, D	Adsorption/desorption of H_2 on Si(100) using quantum Monte-Carlo	5
C. Molteni (U Cambridge, UK)	M. Parrinello (MPI Stuttgart, D)	Phase transformations in nanocrystals, photoreactions	8
B. Ujfalussy (U Budapest, H)	B. Gyorffy (U Bristol, UK)	Quantum wires, oscillatory exchange coupling, domain walls	8
M. Miao (U Antwerp, B)	J.L. Martins (U Lisbon, P)	Pseudopotential codes, GGA implementation	8
D. Ködderitzsch (U Halle/Saale, D)	W. Temmerman (Daresbury Lab.)	Electronic structure of transition metal oxides	25
E. Sjöstedt (U Uppsala , S)	M. Scheffler (FHI Berlin, D)	Training on FLAPW and FHI98 codes	4
R. Grohmann (U Wien, A)	S. Blügel (FZ Jülich)	CeO_2 surfaces, FLEUR code development	5
T. Korhonen (TU Helsinki, SF)	S. Blügel (FZ Jülich)	FLEUR code development	5
E. Wachowicz (U Wroclaw, PL)	M. Scheffler (FHI Berlin)	Structure of Mg(0001) and Be(0001) surfaces	30
S. Shallcross (U Bristol, UK)	I. Abrikosov (U Uppsala, S)	Compositional order and disorder at surfaces of fcc alloys	90

5.2 Reports on Workshops

Conference Scientific Report about the

5.2.1 EUROPEAN RESEARCH CONFERENCE

on Electronic Structure of Solids and Surfaces:
Challenges in predictive descriptions of reaction dynamics and growth properties at surfaces
Lenggries (Bavaria), Germany, 18-23 September 1999

Chairperson:	**Axel Groß** (TU Munich, Germany)
Vice-Chairpersons:	**Gianfranco Pacchioni** (University of Milan, Italy)
	Thorsten Klüner (FHI Berlin, Germany)

The theoretical description of reactions and growth properties at surfaces is an important research field owing to its fundamental aspects as well as its technological relevance. For a predictive description of processes at surfaces the reliable determination of the interaction of atoms and molecules with surfaces is a prerequisite. Due to the improvement of electronic structure theory algorithms and the increase in computer speed in the last years there has been tremendous progress in mapping out whole potential energy surfaces for these processes. The main goal of this conference was therefore to bring together experts in the field of electronic structure theory calculations with theoreticians who work in the field of reaction dynamics and growth processes at surfaces. More specifically, the aim was to review the current status of the field and to inspire fruitful collaborations between these two groups of scientists which used to be rather separate in the past. Equally important for the theoretical treatment of processes at surfaces is the close contact to the experiment. Hence another significant aspect of this conference was the participation of experimentalists working in this field.

To set the stage, the conference was opened with a session on fundamental aspects of electronic structure calculations and density functional theory (DFT). The reliability of DFT calculations is mainly determined by the accurate treatment of the many-body effects. Axel D. Becke (Queen's University, Kingston, Canada) discussed the construction of non-local exchange-correlation functionals. In the construction of these functionals there is still some variational freedom, a fact that was also pointed out later in the conference by Bjørk Hammer (Aalborg University, Denmark). Axel Becke prefers to use this freedom to adjust a small set of variational parameters in order to reproduce a set of known results, but there are other schools of thought that avoid to use any adjustable parameters. Furthermore, the extension of DFT to treat polarizabilities and excited states is of strong current interest. Two possible methods, time-dependent density functional theory and the GW approximation were presented by Evert Jan Baerends (Vrije Universiteit Amsterdam, The Netherlands) and Rex Godby (University of York, UK), respectively. Although these methods can be quite successful for small systems, the determination of electronically excited states for extended systems still represents a considerable challenge.

DFT calculations only provide the potential energy for a set of discrete configurations. In dynamical simulations, however, a continuous representation of the potential energy surface (PES) is needed. The talks of Doug Doren (University of Delaware, USA) and Horia Metiu (University of California at Santa Barbara, USA) were concerned with schemes for the interpolation of *ab initio* energies. A neural network model for inter-atomic interactions was presented by Doug Doren, while Horia Metiu introduced a directed genetic programming scheme for finding the best analytical fit to a set of given data. Both schemes are rather successful in reproducing the PES for low-dimensional problems, however, their applicability for problems with a large number of freedoms (say, more than 10) still has to be proven.

The sessions covering methods for the application of *ab initio* data to simulate processes on surfaces were opened by Geert-Jan Kroes (Leiden University, The Netherlands). He showed that the benchmark system for the activated dissociation of molecules at surface – H_2/Cu – can now be treated in a detailed manner by six-dimensional quantum dynamics methods using a PES derived from DFT calculations. These calculations allow a quantitative comparison with experiment so that also the accuracy of the DFT-derived PES can be checked. Didier Lemoine (Université de Lille, France) demonstrated the importance of the high-dimensionality in the simulation of scattering processes by showing that the so-called supernumerary rotational rainbows which appear in low-dimensional simulation of NO scattering from Ag(111) disappear if also the surface corrugation is considered.

The first talk in the session about growth and etching, corrosion and lubrication was given by Harald Brune (EPF Lausanne, Switzerland). He reviewed the field of STM experiments to study nucleation and growth on homogeneous and inhomogeneous substrates. Due to the atomic resolution of the STM, these experiments can yield a detailed information about the microscopic processes, in particular if the experiments are combined with *ab initio* calculations. The theoretical treatment of atomic growth processes was the topic of the talk by Talat Rahman (Kansas State University, USA). She stressed the importance of finite temperature effects in the simulation of growth processes. For many systems the fact what are the most favourable processes at a certain surface temperature is determined by the Free Energy which includes entropic effects and not just by the bare barrier heights. This session was closed by the talk of Anne Chaka (Lubrizol Corp., USA) with the provocative title *Quantum Mechanics and the Automobile*. She demonstrated that nowadays DFT is already used by the chemical industry to illuminate the chemical processes underlying the performance of lubricants and additives.

There is one main difference between chemical reactions at surfaces and in the gas phase: at surfaces energy can be very efficiently dissipated by excitation of phonons or electron-hole pairs while in the gas phase there are usually no dissipation channels open. However, the theoretical treatment of dissipation, in particular within a quantum mechanical framework, still represents a major computational challenge. Two complimentary approachs were discussed by Ronnie Kosloff (Hebrew University, Jerusalem, Israel) and Shiwu Gao (Chalmers University, Göteborg, Sweden). Ronnie Kosloff introduced a finite surrogate Hamiltonian to generate the true short time dynamics of a primary system coupled to a bath. Using the resurfacing of hydrogen to a Ni surface he demonstrated the applicability of this approach if the temperatures are not too large and the time scales are not too long. Shiwu Gao, on the other hand, presented a dissipative quantum dynamics method within the reduced density matrix formalism. This method, which can deal with high temperatures but is still restricted to low dimensions, was applied to the photoinduced reaction of O_2 on Pt(111). An alternative approach to determine reaction rates in thermal equilibrium situations was presented by Hannes Jónnson (University of Washington, Seattle, USA). He focused on quantum transition state theory in terms of Feynman path integrals and its application to H_2 dissociative adsorption.

As already mentioned above, the determination of electronically excited states still represents a major challenge. But equally challenging is the inclusion of electronic transitions in the simulation of reaction dynamics. The semiclassical treatment of electronic transitions in molecular dynamics simulations was the topic of the talk by John Tully (Yale University, New Haven, CT, USA), while Peter Saalfrank (University College London, UK) presented a quantum mechanical description of desorption processes induced by electronic transitions. The semiclassical treatment can easily be extended to higher dimensions but treats the electronic transition only in an approximative manner. The quantum mechanical description, on the other hand, can treat the electronic transition properly, but is still limited to low dimensions. The contact to experiment in this session was provided by Katharina Al-Shamery (Universität Oldenburg, Germany) who gave a detailed report on laser induced desorption experiments from oxide surfaces.

Dave King (University of Cambridge, UK) presented molecular beam experiments of important catalytic processes on Pt surfaces. He also emphasized the important role that DFT calculations can play in combination with experimental results for a microscopic understanding of these processes. This was furthermore demonstrated in the talk by Notker Rösch (Technische Universität München, Germany) who focused on oxide supported metal species investigated by DFT calculations using the cluster approach to represent the surface. Bjørk Hammer (Aalborg University, Denmark) showed that the reactivity at stepped surface can be enhanced dramatically compared to flat surfaces. He demonstrated how this enhanced reactivity can be understood microscopically by carefully analyzing DFT results. As already mentioned above, he also pointed out that there is an intrinsic uncertainty in the construction of the exchange-correlation functional in the generalized gradient approximation which can lead to changes of up to 0.3 eV in the barrier heights of the reactions he considered. The last talk of the conference was given by Mario Rocca (University of Genova, Italy) who showed experimentally how complicated the seemingly simple system oxygen on Ag(100) can be.

The talks were supplemented by two poster sessions. All posters were introduced by a three-minute, one-slide presentation which was well received. The conference was closed by concluding remarks of Volker Heine (Cavendish Laboratory, Cambridge, UK). He emphasized the tremedous progress that has been made in the last years in DFT calculations as far as the size of the systems that can be treated is concerned. This was especially reflected in the posters that were presented at the conference. DFT calculations have become an indispensable tool in the theoretical treatment of reaction dynamics and growth processes at surface. Still there are many open problems, in particular in the treatment of electronically excited states, as was demonstrated in this conference. In this field the experimentalists are far ahead of the theoreticians.

Overall it seems that bringing together experts from different fields at this conference was quite a success. The nice atmosphere in the Arabella Brauneck Hotel in Lenggries which allowed many relaxed and informal scientific discussions certainly contributed to this success. The excursion to Munich was also an excellent opportunity to get to know each other, in some cases with unexpected results. Last but not least, the smooth preparation of the conference by the EURESCO staff in Strasbourg, in particular Rhona Heywood, was very important for the success of the meeting. Hopefully many fruitful collaborations will originate from this conference. Since DFT calculations represent such an versatile tool to investigate microscopic details in the interaction of atoms, molecules and solids, it is desirable that the EURESCO series *Electronic Structure* will be continued in the future, probably visiting other fields like biological systems, coherent control or semiconductor technology, just to name a few.

Abstracts of the Invited Talks

(in chronological order according to the program)

Non-Local Exchange-Correlation Functionals

Axel D. Becke

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

Evidence is mounting that so-called "hybrid" exchange-correlation density-functional theories (that is, including an exactly computed exchange component) are superior to purely local DFTs. Unfortunately, exact computation of exchange is costly, especially in the plane-wave methodologies widely used in the physics community. We will discuss an approximate way to treat the multicentre nonlocality of exact exchange using a new local variable related to the kinetic energy density. The outcome is a purely local exchange-correlation DFT which performs almost as well as its parent hybrid DFT on atomization-energy tests.

Moreover, plots of this new variable contain remarkable chemical information, clearly revealing shell structure, bonding and lone electron pairs, multiple bonds, etc. This function may surpass ELF (the "electron localization function") of Becke and Edgecombe for its chemical utility.

Implementation of time-dependent DFT and application to response properties of molecules

E.J. Baerends

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The Netherlands

The development of time-dependent DFT allows, within the context of density-functional theory, the calculation of response properties of molecules (polarizabilities, hyperpolarizabilities, excitation energies). An efficient implementation [1] is possible using similar computational techniques as applied before for ground state calculations. The quality ofthe calculated response properties of molecules depends in TDDFT on the Kohn-Sham one-electron potential and its functional derivative with respect to the density, the exchange-correlation kernel. We will demonstrate that it is possible to model these functionals with sufficient accuracy so that quite accurate response property calculations can be performed with TDDFT for small organic molecules [2], as well as for transition metal complexes. However, for conjugated chains, which are particularly interesting from the point of view of non-linear optics, the LDA and GGA approximations fail rather miserably for the (hyper)polarizability [3]. This confirms earlier findings by solid state physicists that a stronly nonlocal contribution to the KS potential, which builds a counteracting potential to the applied one, is absent from the LDA and GGA models.

[1] S.J.A. van Gisbergen, J.G. Snijders & E.J. Baerends Implementation of time-dependent density functional response equations Comput. Phys. Comm 118 (1999) 119

[2] S.J.A. van Gisbergen, V.P. Osinga, O.V. Gritsenko, R. van Leeuwen, J.G. Snijders & E.J. Baerends, Improved density functional theory results for frequency-dependent polarizabilities, by the use of an exchange-correlation potential with correct asymptotic behavior, J. Chem. Phys. 105 (1996) 3142-3151

[3] S.J.A. van Gisbergen1, P.R.T. Schipper, O.V. Gritsenko, E.J. Baerends, J. G. Snijders, B. Champagne and B. Kirtman, Electric field dependence of the exchange-correlation potential in molecular chains, Phys. Rev. Lett. 83 (1999) 694-697

Ab initio energies for excited states

R.W. Godby

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I shall review the contrasting and complementary roles of density-functional theory (DFT) and *ab initio* many-body perturbation theory (MBPT) in condensed-matter physics, with particular reference to surfaces and surface dynamics.

Our *ab initio* MBPT work is based on Hedin's GW approximation, and uses our recent "space-time" method [1], in which the Green's function G and the screened Coulomb interaction W are represented in the real-space and imaginary-time domain, increasing the efficiency of the calculation of W and the self-energy Σ, and its scaling with system size. The availability of the full self-energy $\Sigma\left(\mathbf{r}, \mathbf{r}', \omega\right)$ gives access to such quantities as the electron density and total energy, in addition to quasiparticle energies and the spectral function.

An application to the Al(111) surface [2] will be presented. The GW self-energy automatically includes the image potential not present in any local-density approximation for exchange and correlation. We solve the energy-dependent quasiparticle equations to obtain surface state wavefunctions, and calculate the effective local potential experienced by electrons in the near-surface region.

I shall also present the results of studies using Hubbard model systems [3] (for which exact results may be calculated), which address the accuracy of the GW approximation, and candidate extensions beyond GW for more strongly correlated electrons, for the spectral function, total energy, etc.

Further references and papers are available at
`http://www-users.york.ac.uk/~rwg3/talks.html`.

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Neural Network Models of Inter-Atomic Interactions: Chemical Dynamics and Thermodynamics from First-Principles Calculations

Doug Doren

University of Delaware, Newark, Delaware, USA

Classical or quantum simulations of dynamics and thermodynamics all require a representation of the inter-atomic interaction potential. Traditional empirical model potentials are not accurate enough to provide reliable insight in many cases, such as chemically reacting systems. It is now practical to perform accurate calculations of the energy and inter-atomic forces directly from the Schrodinger equation. However, full simulations of reaction dynamics with an accurate solution of the Schrodinger equation at each time step are very costly (in computational terms) and may not be applicable to problems that require long time scale simulations or large numbers of trajectories to achieve adequate statistical sampling.

This talk will describe the use of feed-forward neural networks to create a potential function by interpolating among a data set of energies and forces calculated from a first-principles method at a finite set of atomic configurations. The neural network model is an analytic functional form, differentiable and defined at arbitrary configurations, that requires no assumptions about the form of the interaction potential. With suitable training (i.e., parameter fitting), neural networks can reproduce energies to "chemical accuracy" (errors < 0.1 electron volt). The time to evaluate the energy and forces with the neural network model is several orders of magnitude less than direct solution of the Schrodinger equation. The neural network method appears to work well even for rather complex interactions, such as those occurring near transition states.

The method can be applied in a variety of ways. All applications in the current literature have generated energies at a set of geometries from first-principles calculations, trained a network to reproduce that data, and used the resulting network potential model in a simulation without further recourse to first-principles calculations (just as one might use an empirical potential). On the other hand, the method can be used in a scheme to accelerate a first-principles molecular dynamics simulation, solving the Schrodinger equation at each time step, but using the neural network to improve sampling near a transition state. This talk will describe the problems in trying to develop model potentials from first-principles calculations, the reasons one might choose to use neural networks, the training procedures used, the quality of the neural network model predictions and some applications. Related work from other research groups will also be reviewed.

Applications of genetic programing and stochastic Schrödinger equations to problems in quantum mechanics

D. Makarov and H. Metiu

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We present two recent ideas that concern solving Schrödinger equation. One formulates the time independent Schrdinger equation as an optimization problem and then uses genetic programming to find a function that minimizes the error. A brute force application of genetic programming turns out to be extremely inefficient. The use of a directed genetic algorithm allows us to solve simple problems. The method provides analytic solutions of the Schrödinger equation. At this early stage in its development, we cannot assess if the method will be competitive in high dimensionality problems. We feel however that it deserves further study. In the second part of the talk we present a method for introducing dephasing in the stochastic Schrödinger equation algorithm of Dalibard, Castin and Mølner. The procedure is used to discuss a coherent pump-probe experiment performed by Scherer, Jonas and Fleming. This method is often more efficient than using the time dependent density matrix and is able to describe the stochastic phenomena encountered in single molecule spectroscopy.

Six-dimensional Quantum Dynamics of Dissociation of H_2 on Cu(100)

G.J.Kroes

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Six-dimensional (6D) quantum dynamical calculations have been performed on the reaction of $(v = 0, j = 0)$, $(v = 1, j = 0)$, $(v = 0, j = 4)$, and $(v = 1, j = 1 - 3)$ H_2 with Cu(100). A 6D potential energy surface (PES) [1] was used that was obtained from density functional theory (DFT), using a Generalized Gradient Approximation and a slab approach.

Comparison of the 6D results to experiment suggest that the barriers in the PES are too high by ~ 0.1 eV [2,3], but the vibrational efficacy (0.62) is in excellent agreement with experiment (0.63) [4]. In agreement with associative desorption experiments on H+ Cu(111) [5], the predicted quadrupole alignment of $(v = 0, j = 4)$ H_2 desorbing from Cu(100) is a decreasing function of the desorption energy, for the range of energies for which experiments are available for Cu(111). Results for vibrational excitation of H_2 from the $(v = 0, j = 0)$ and $(v = 0, j = 4)$ state strongly suggest that the rotational cooling that has been observed to accompany vibrational excitation in experiments on Cu(111) [6] is due to j decreasing on average in collisions leading to vibrational excitation. An alternative mechanism, in which j is conserved and vibrational excitation is less likely for high j, could be ruled out with certainty [7].

Results of 6D classical trajectory calculations are in reasonable agreement with fully quantal calculations for higher translational energies [8]. A surprising result of the CT calculations is that the site on which reaction occurs at low energies is highly dependent on the initial rotational state of H_2.

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Wave packet dynamics of the rotational rainbow scattering of NO from Ag(111)

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The rotationally inelastic scattering of NO molecules from the Ag(111) surface has been extensively studied both experimentally and theoretically . It is facilitated by the fact that the surface interaction is weakly destructive and chemisorptive. Notably, Rettner, Kimman and Auerbach (RKA) on one hand, and Geuzebroek et al. on the other hand, have reported high resolution investigations of this system for unoriented [1] and Stark-oriented [2] NO beams. Meanwhile De-Pristo and Alexander [3] have derived a complete set of potential energy surfaces (PESs) within the corrected effective medium theory and the NO rigid rotor assumption. Their semi-empirical approach consider the surface corrugation as well as the open shell character of NO in its ground state, and one can thus expect a semi-quantitative description of the interaction.

I will present the results of large scale quantum calculations taking explicitly into account both the surface corrugation and the two PESs of distinct electronic symmetry required to describe collisions of either unoriented [4] or Stark-oriented [5] NO molecules with Ag(111). The DePristo and Alexander PESs [3] were used as well as a time-resolved analysis of the NO-axis distribution. I will discuss the rotational rainbow structures, the necessity of the two electronic PES representation, the role of surface corrugation, the orientational steering propensities and the steric effects, in relation to the experimental measurements [1,2].

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Monitoring growth processes on metals: Growth Kinetics on Inhomogeneous Surfaces

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Variable temperature (VT) STM studies of nucleation and growth have been invaluable in clarifying and quantifying nucleation and growth processes on isotropic and defect free (homogeneous) surfaces [1]. The talk will review this work briefly, before proceeding to discuss recent work on inhomogeneous substrates.

Inhomogeneous substrates are surfaces with dislocations, moir patterns or point defects. We will show experiments that enable access to the potential energy surface experienced by metal atoms diffusing over such substrates. These measurements reveal that partial surface dislocations in (111)-oriented fcc metal substrates often are strongly repulsive line defects. Dislocation networks resulting from strain relief in heteroepitaxy can therefore be used as template for the self-organized growth of nanostructure arrays. The approach will be demonstrated for Fe and Co forming a hexagonal grid of dots with 3.6 nm period on 2ML Cu/Pt(111).

The nucleation kinetics of Pd on MgO(100) is indicative for nucleation at attractive point defects. The temperature dependent cluster densities derived from VT-AFM, in conjunction with mean-field nucleation theory, give estimates of the trapping and cluster binding energies. Comparison to ab-initio calculations reveals the possible microscopic origin of the trapping sites.

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Atomic Processes in Growth at Metal Surfaces*

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A microscopic study of processes that control growth at solid surfaces is invaluable as it ultimately relates to the nature of the bonding between atoms in regions of low symmetry and coordination and provides an understanding of how the bonding and the processes vary with temperature. In this regard I will present results of systematic, theoretical studies of defects like steps, kinks, vacancies, adatoms, and 2-D island clusters that contribute to epitaxial growth on the (111) and (100) surfaces of several transition metal surfaces. Particular focus will be on a comparative study of two types of steps and triangular islands on the (111) and steps on the (100) surfaces. By examining the temperature dependent relative stability of these structures (size dependence also for the 2-D islands), and the strengths of the Schwoebel barriers at step edges and corner, I will show that vibrational entropy makes an essential contribution. These calculations are performed with many body interatomic potential, as obtained from the embedded atom method, and results are compared with those from first principles electronic structure calculations, and experimental data, where available. A key ingredient in the calculations, the local vibrational density of states, is evaluated using a real-space Green's function method. The local thermodynamic properties of the systems are then calculated in the harmonic approximation of lattice dynamics. The temperature dependent energetics and stability of specific defects are thereby extracted through considerations of the free energy. We find the characteristics of the atoms of different coordination numbers to be influenced significantly by their local environments [1]. Through considerations of the calculated diffusion coefficients for adatoms and vacancies along specific directions in the vicinity of steps and kink-sites, I will discuss the implications for epitaxial growth on Cu(100) and Ag(100) [2]. These studies enable us to produce a unified picture of the relationship between force fields, dynamics, stability and atomic coordination.

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Quantum Mechanics and the Automobile: Tailoring the Reactivity of Sulfur for Lubricant Applications

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For over 50 years, organosulfur compounds have been added to lubricating oils to protect ferrous metal surfaces via the formation of sacrifical layers of ironsulfide. Many organosulfur compounds can, however, also lead to corrosion of copper-containing metal alloys such as bronze and brass. This is a serious limitation as both ferrous and non-ferrous metals are commonly used to fashion different parts of the same mechanical system. Optimizing the performance of organosulfur compounds to maximize antiwear performance and minimize copper corrosion can benefit from an understanding of these processes at the atomistic level. Calculations based on Density Functional Theory are used to investigate the properties of several polymorphs of ironsulfide surface boundary layers, as well as three possible mechanisms of copper corrosion. Implications of these results with respect to the relationship between the chemical structure of the sulfides and their performance are discussed.

Surrogate Hamiltonian for Dissipative Dynamics

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Dissipative dynamics of an adsorbates near a metal surface is formulated consistently by replacing the infinite system-bath Hamiltonian by a finite surrogate Hamiltonian. This finite representation is designed to generate the true short time dynamics of a primary system coupled to a bath. A detailed wavepacket description is employed for the primary system while the bath is represented by an array of two-level-systems. The number of bath modes determines the period the surrogate Hamiltonian reproduces the dynamics of the primary system. The convergence of this construction is studied for the dissipating Harmonic oscillator and the double-well tunneling problem. Converged results are obtained for a finite duration by a bath consisting of 4-11 modes. The formalism is extended to dissipation caused by electron-hole-pair excitations. The stopping power for a slow moving proton is studied showing deviations from the frictional limit at low velocities. The method has been applied to diffusion of hydrogen on the surface of a Ni crystal and in the bulk.

Dissipative Quantum Dynamics at Surfaces

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This paper discusses the role of electronic dissipation in the dynamical processes at surfaces. We start with an explicit example, photoinduced reaction of O_2 on Pt(111), and demonstrate various difficulties encountered in coherent wavepacket (CWP) dynamics, due to lack of dissipation. A general Lindblad approach for dissipative quantum dynamics (DQD) with linear[2] and nonlinear[3] coupling is then presented and discussed in detail. As the first example of application, this approach is used to describe the same system. We show that DQD overcomes all the difficulties encountered by CWP. In particular we demonstrate how the anisotropic dissipation of a 2-D system, here the molecule-surface bond and intra-molecular bond sensitively determines the branching ratio between desorption and dissociation. Finally, outlooks to other related dynamical processes are also discussed in the context of dissipative quantum phenomena at surfaces.

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Statistical methods in the description of reaction at surfaces: Development of Quantum Transition State Theory and Application to H_2 dissociative adsorption

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In most practical situations, the important question in gas-surface dynamics is how likely a molecule in a gas phase (typically at high pressure) will stick on a surface or desorb from a surface. When the gas and surface have the same temperature, the adsorption rate as well as the desorption rate can be calculated in many cases to a good approximation with transition state theory.

While classical transition state theory is well established, a great deal of effort has recently been devoted to the development of a quantum mechanical version of transition state theory, in particular where quantum statistics are formulated in terms of Feynman Path Integrals. A theory and computational methodology will be presented where the quantum transition state is defined as a conical dividing surface in the full space of all closed paths in the Feyman Path Integral formulation of the free energy. A 'reaction path' is taken to be the minimum action path (analogous to the minimum energy path in classical systems) through this space and is used to parametrize the progression of the system. The free energy at the transition state is calculated by accumulating the reversible work needed to shift the system from reactants towards products. The method is applicable to large systems including many quantum and classical degrees of freedom. At low temperature, in the harmonic limit, the method gives the same results as the stationary phase formalism commonly referred to as 'instanton theory'. At high temperature (above the crossover temperature) the theory reduces to the centroid density approximation, and the method becomes classical variational transition state theory in the classical limit. Results will be presented for model systems and for dissociative adsorption and desorption of H_2 molecules at the Cu(110) surface. A method for finding and evaluating the instanton directly from first principles calculations of the total energy and atomic forces (for example from plane wave DFT calculations) will be discussed.

This work was carried out in collaboration with Greg Mills (UW), Greg Schenter (PNNL) and Dimitrii Makarov (PNNL, now at UCSB).

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Both papers are available at
`http://www-theory.chem.washington.edu/~hannes/publicationsQTST.html`

Molecular Dynamics with Electronic Transitions

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Molecular dynamics (MD) simulations have been very valuable in elucidating the dynamics of chemical processes at surfaces. MD is based on the Born-Oppenheimer approximation; nuclear motion is assumed to evolve on an adiabatic potential energy surface corresponding to a single electronic state, usually the ground state. However, there are many situations for which electronic transitions play an important role. Nuclear motion induces electronic transitions which, in turn, change the forces exerted on the nuclei.

A unified approach toward treating electronic transitions and nuclear motion self-consistently within a MD framework will be presented. Methods will be illustrated by applications to adsorption and energy exchange at metal surfaces.

Quantum Mechanical Description of Desorption Induced by Electronic Transitions

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Adsorbate-surface bonds can not only be broken thermally, but – more selectively and possibly with atomic resolution – also with scanning tunnelling microscopes (STMs) and (ultrashort) laser pulses. The microscopic unravelling of the basic mechanisms of bond-breaking at surfaces is of interest for fundamental research (dynamics of open quantum systems, non-adiabatic transitions), but also for applications (selective photochemistry, microstructuring of materials).

In this contribution we describe quantum-dynamical simulations for ultrafast bond-breaking enforced by STMs and lasers, which lead to the desorption of atoms or molecules from semiconductor or metal surfaces. Mostly we will concentrate on DIET (Desorption Induced by Electronic Transitions) or DIMET ("M"="Multiple"). We use time-dependent density matrix theory and solve Markovian Liouville-von Neumann equations for open quantum systems to elucidate (i) basic mechanisms and timescales, (ii) effects of thermal or photochemical vibrational preparation of the reactants, (iii) isotope effects, and (iv) possibilities and limitations for the active control of DIET and DIMET [1]. As examples we study indirect (substrate-mediated) photoinduced DIET of NH_3 (ND_3) from Cu(111) and NO from Pt(111), and direct STM- and direct laser-induced DIET of H(D) from Si(100). Methodological aspects for the solution of the underlying open-system equations of motion will be addressed [2].

Finally, for the example system NH_3/Cu(111) photo- or STM-induced chemistry proceeding exclusively in the ground electronic state (of the adsorbate-surface complex) will be studied.

Using static or slowly varying electric fields, adspecies can be desorbed with high efficiency. But also other “reactions” such as the vibrational excitation, the isomerziation, and the adsorption of molecules at surfaces should be possible in this way [3].

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Laser induced desorption experiments from oxide surfaces

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Photochemistry from oxide surfaces is very often characterised by a pronounced efficiency in contrast to photochemistry from metal surfaces [1]. On the other hand it is known that metal clusters of a few Ångstrøm size exhibit unique strongly size dependent properties with respect to their electronic structure as well as morphology. Interaction with a solid support can furthermore modify clusters substantially resulting in drastic effects on the interaction between clusters and adsorbates. Thus nano-sized transition metal clusters belong to an important class of substances in catalysis. Only recently first steps towards a deeper understanding of properties of metal aggregates on oxidic supports could be achieved [2]. It has been found among other things that cluster size as well as morphology can be influenced by choosing the proper growth conditions during vapour deposition of metal atoms on a solid surface.

We shall present first experiments on the cluster size dependence of the UV-laser induced photochemistry at 6.4 eV of CD_4 and NO adsorbed on Pd aggregates deposited on an epitaxial film of Al_2O_3 on NiAl(110). Cluster sizes were ranging between less than 10 Å up to more than 75 Å according to the growth conditions. This size regime is of particular interest as quantum size effects may occur for the smaller clusters while the larger clusters still are small compared with the mean free path of the electrons. In case of CD_4 we found a strong cluster size dependence in the ratio of photodesorption to photodissociation [3]. Photodesorption was particular efficient for the small clusters while a detection limited threshold was observed for photodissociation at a cluster size of around 37 to 49 Å of diameter. Only for the largest clusters the photodissociation cross section was approaching the bulk value. However, poisoning effects on quenching the photodissociation which are caused by methyl adsorbates occur at much lower concentrations even for the largest clusters as compared to the bulk crystals.

For NO the situation is more complex. On Pd(111) different chemisorbed species can be observed, none of which is photoactive at 6.4 eV. For the clusters investigated only the one with the lowest desorption temperature around 240 K is observed in thermal desorption spectra except for clusters above 70 Å. A further physisorbed species at 160 K occurs in thermal desorption spectra with increasing concentration at decreasing cluster size which has not been observed before for bulk crystals. In infrared spectra this species is not observable. In contrast to the bulk photodesorption has been observed for both species. Again the photodesorption probability for both species increases dramatically with decreasing cluster size. However, the photodesorption efficiency is up to three orders of magnitude larger for the physisorbed species. Quantum state selective detection of the desorbing species revealed that final state distributions are increasingly hot for the physisorbed species with decreasing cluster size. Final state distributions resulting from desorption of the chemisorbed species are less sensitive to the cluster size.

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Dynamics of Catalytic Reactions

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Quantitative studies of processes at solid surfaces have finally emerged to the point where even reasonably complex systems can yield to detailed experimental analyses. Here I plan to review recent progress in my group in tackling several important catalytic processes [1,2].

The Ostwald reaction, ammonia oxidation to NO over Pt surfaces, has been studied using molecular beams [3,4,5], and temperature-programmed reflection-absorption infrared spectroscopy [6]. Using conclusions derived from single crystal adsorption calormetry [7], a new mechanism has been proposed for the biphasic production of NO or N_2. This has implications for industrial practise.

Methane partial oxidation to CO and H_2, a mixture known industrially as syngas which is readily catalytically converted to methanol, is a potentially important reaction in the oil industry. Detailed analyses of both the dissociative adsorption of CH_4 on Pt{110} [7] and the dissociation of O_2 [8] using supersonic beams will be described. In addition the reactions of adsorbed C [9] and adsorbed CH [10] with O_2 have been examined, producing a coherent model for the overall reaction of CH_4 with O_2 on Pt {110}(1x2).

This growing database from experimental studies on well-defined systems can be extended by direct modelling, exploiting recent advances in DFT-GGA slab calculations. This will be illustrated with two examples: experiment-theory comparisons for the chemisorption and dissociation of ethylene on Pt{111} [11], and a new model for the reaction intermediate for the Fischer-Tropsch reaction between H_2 and CO with coadsorbed K on Co [12].

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Reactions on oxide surfaces:
Computational Studies of Supported Transition Metal Species: Towards Reactions at Surfaces

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The bonding of transition metal atoms and clusters to oxide support has been investigated computationally using a density functional method based on cluster models. Examples will be shown for the adsorption at ideal and defect sites of Mg(OO1). Naked as well as ligated adsorbates will be discussed. Based on these model studies a critical evaluation of EXAFS results for clusters on oxide and zeolite supports will be given. Finally, we will discuss recent experiments on acetylene trimerization at MgO-supported Pd species.

Reactions of NO on flat and stepped metal surfaces:
Bond activation at mono-atomic steps:

NO dissociation at corrugated Ru(0001)

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The NO bond activation at a corrugated Ru(0001) surface is investigated using density functional theory. Mono-atomic steps in the Ru surface are found to offer completely new reaction pathways with highly reduced energy barriers compared to reaction at a flat surface. The calculated energy barriers are found to be dominated by final state effects. The favorable barriers at the step edges result from the attractive chemisorption potential energies of the non-interacting reaction products, atomic N and O, and from a minimal degree of intra-molecular repulsion mediated through the substrate. The sensitivity of the numerical results to the choice of exchange-correlation functional is considered. A key property determining this sensitivity is found to be the area of iso-electron density surfaces around the initial, transition, and final state configurations.

Alternative pathways for oxygen dissociation: Reactive, non-reactive and subsurface phases of oxygen on Ag(001)

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Oxygen adsorption on Ag surfaces has attracted the interest of the surface science community for several decades because of the unique selectivity of Ag powders for the catalytic partial oxidation reaction of ethylene. In spite of the effort the nature of the active oxygen species escaped so far identification. In our recent HREELS, XPS and XPD study of the oxidation of Ag(001) we found that the system is extremely complicated as a variety of oxygen moieties can be produced depending on crystal temperature and subsurface oxygen content of the sample. A moiety with an XPS O1s binding energy of 530 eV forms when dosing is performed below room temperature. It involves a missing row reconstructed substrate and it is stabilized by the presence of oxygen in the immediate subsurface region. This phase converts to oxygen with a O1s binding energy of 528 eV when the reconstruction is removed by annealing above 350 K. At the phase transition part of the oxygen adatoms dissolve into the bulk and the signal corresponding to subsurface atoms disappears. The 528 eV species is active towards CO oxidation and total C2H4 oxidation, while the low temperature phase is inert and could therefore play an important role in the partial oxidation reaction of ethylene. Similar oxygen moieties were indeed identified for Ag samples oxidised at atmospheric pressure (X.Bao et al. Phys. Rev. B 54, 2249). The chemically

unreactive phase exists (O alpha, O1s binding energy of 530 eV) was shown to survives up to temperatures of 700 K and to be therefore present under industrial reaction conditions. We suggest that the stability at higher temperatures is due to the larger concentration of dissolved oxygen. When cooling Ag(001) below room temperature the reconstructed phase is restored and the O1s binding energy moves back to 530.3 eV. The process is ignited when the subsurface oxygen concentration reaches a certain threshold due to oxygen segregation from the bulk. The time constant of the backconvertion process as well as the chemical reactivity towards CO of the high temperature phase depend on the subsurface oxygen content of the sample. CO pressure is observed to accelerate the kinetics of the convertion process below room temperature. The two oxygen moieties could also be produced by impact induced dissociation.

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Potential Energy Surfaces for **ab initio** *Molecular Dynamics Simulations : A Neural Network Fit*

28. M.V. Mamonova
Calculation of Surface and Adhesion Characteristics of Metals and Their Liquid Phases

29. Giuliana Materzanini, Peter Saalfrank and Philip J.D. Lindan
Quantum Size Effects in Thin Lead Films: A First-Principles Study for Pb(111) Slabs

30. A. Michaelides and P. Hu
A comparison between CH_3 *hydrogenation and dehydrogenation on Ni(111)*

31. R. Milot and A.P.J. Jansen
Wavepacket Simulations of the Vibrational Scattering of Methane

32. Y. Morikawa, K. Iwata and K. Terakura
Ab Initio Study of Methanol Synthesis over Zn-deposited Cu Surfaces

33. Maziar Nekovee and W.M.C. Foulkes
Quantum Monte Carlo Analysis of Exchange and Correlations in the Strongly Inhomogeneous Electron Gas

34. Tsukuru Ohnaki
Electric Field Effect of Adsorption and Charge Transfer at Metal Electrode Surfaces

35. Roar A. Olsen
Atomic and Molecular Hydrogen Interacting with Pt(111)

36. N. I. Papanicolaou, G. A. Evangelakis, D.G. Papageorgiou
Tight-binding interatomic potential for Al and molecular-dynamics study of self-diffusion on Al(100) surface

37. Uri Peskin and Michal Steinberg
A Temperature-Dependent Schrödinger Equation Based on a Time-Dependent Self-Consistent Field Approximation

38. Kharissia Pettus and Andrew Kummel
Remote Dissociation and Chemical Selectivity - ICl/ Al (111)

39. E. Pijper
Diffraction of p- and n-H_2 *from LiF(001)*

40. Karsten Reuter, M. Veronica Ganduglia-Pirovano, Catherine Stampfl, and Matthias Scheffler
Surface Core Level Shifts of O Superstructures on Ru(0001) and Rh(111)

41. Arno Schindlmayr
    The GW approximation as a tool for calculating excited-state potential-energy surfaces
42. Ari P Seitsonen and Herbert Over
    Co-Adsorption of Adsorbates on Transition Metal Surfaces
43. H.U. Suter and T. Greber
    Wave–packet calculations for a reaction after charge transfer: $N_2O + e^- \rightarrow N_2 + O^-$
44. F.T. Umarova, Z.M. Khakimov, N.T. Sulaymonov *Effects of Charge Localisation at Semiconductor Surfaces on Equilibrium States and Emission of Atoms*
45. H.N. Yeritsyan, A.A.Sahakyan, S.K. Nikogosyan, A.S. Hovhannisyan,
    E.A. Hakhverdyan
    Study of Electronic States in Solids with Point Structural Radiation Defects

5.2.2 Report on CECAM ”Electronic excitations” Workshop

CECAM WORKSHOP “CALCULATION OF ELECTRONIC EXCITATIONS IN FINITE AND INFINITE SYSTEMS”

Sponsored by CECAM and by the European Science Foundation Programme ”Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces” (Psi-k)

Organised by **Lucia Reining**, Ecole Polytechnique, France
Giovanni Onida, University “Tor Vergata”, Rome, Italy
Angel Rubio, University of Valladolid, Spain

The aim of this workshop was to bring together researchers of different backgrounds: density functional, many-body, and nuclear physics approaches in order to assess the present status of the ab-initio computation of electronic excitation spectra, and to make connection with up-to-date characterizations by experimental spectroscopies: photoemission (single and two-photon, inverse and time resolved), photoabsorption, electron-energy-loss, scanning-tunneling-microscopy, near-field, etc.. The will to build up a strong community has been demonstrated by three facts which have characterized this workshop: First, the number of participants has been considerably bigger than the number of invited speakers. A part from the 20 invited speakers, more than 20 collegues from many european countries have attended the workshop as audience. This situation had not been particularly encouraged by the organizers, since we had feared that discussions might suffer from the workshop becoming too big, but: Second, especially during the very lively discussions, involving both the speakers and the audience, it could be felt that the links between the various communities are growing, and that the effort which is made in the emerging field of calculations of electronic spectra is actually converging. Third, the PhD students and post docs whose participation was facilitated by the financial support of ESF/Psi-k have felt themselves involved in this process.

The program has been constructed by discussions around several main questions:

a) One-particle excitations: Performance of the GW approach today, calculation of band structures, lifetimes, photoemission. There has been a clear evolution going from GW calculations limited to getting good band gaps towards the use of Green’s functions techniques for the description of more complex properties, like electron/hole lifetimes or image states.

b) Calculation of two-particle excitations: solution of the Bethe-Salpeter equation, optical properties, x-ray absorption. The solution of the two-particle problem has shown to be now feasible for a variety of systems, although the number of theoretical and technical problems to be solved remains non negligeable.

c) Theoretical questions: problems of self-consistency, vertex corrections, description of superconductivity, Berry phase. It has clearly emerged that the problems which keep us busy are not at all limited to computational ones.

d) Comparison of TDDFT (Time-dependent density functional) and Green's functions approaches for the calculation of excited states properties. TDDFT in the adiabatic LDA approximation has turned out to be successful in small systems. A detailed explanation of this success, and its unsuccess in infinite systems, is still missing. A big part of the discussions has been dedicated to the links between TDDFT and Green's functions techniques.

The detailed program, and the abstracts, are attached below. More information can be found on the web page of the workshop: http://www.roma2.infn.it/onida/w99/.

Programme

Wednesday 1 September

09:00 Welcome and Announcements

Chairperson: L. Hedin

09:15 Rex Godby (York)

Introductory talk on the GW method + Developments and applications of the GW space-time method

10:00 Andrzej Fleszar (Würzburg)

Electronic structure of II-VI semiconductors: HF, LDA, EXX and GW calculations

10:45 Patrick Rinke (York)

Image Effects in Small Quantum Dots

10:55 Coffee Break

Chairperson: R.W. Godby

11:20 Carl-Olof Almbladh (Lund)

Vertex Corrections beyond GWA in polarons models

12:05 Brief presentation of the activities of the european groups forming the NANOPHASE research network (network pending EU approval):

Godby(York) - Reining(Paris) - Almbladh(Lund) - Rubio(Valladolid) - DelSole(Rome) - Bechstedt(Jena) - Schindlmayr(Berlin)

13:05 Lunch

Chairperson: S. Louie (Berkeley)

14:30 Pablo Garcia-Gonzalez (York)

Many body GW calculation of the total energy of electron systems

14:50 Paula Friera (York)

Improved Exchange and Correlation Energy Functionals

15:05 Walter Eckardt (Berlin)

Calculated lifetimes of hot electrons in aluminum and the nobel metals using a plane wave basis set

15:50 Coffee Break

Chairperson: A. Rubio (Valladolid)

16:15 Friedhelm Bechstedt (Jena)

Optical properties of large systems: Towards a many-body description

16:50 Ulf von Barth (Lund)

Gradient expansion approximations to the kinetic energy functional

17:35 Lars Hedin (Lund)

On correlation effects in x-ray absorption spectroscopy

18:20 Poster presentations

All participants had the possibility to have a poster exposed during the period of the workshop, as a support for discussions. Each poster was presented by a 3-minutes overview.

Thursday 2 September

Chairperson: R. Del Sole (Rome)

09:15 Lucia Reining (Paris)

Introduction on the calculation of excitonic effects

09:30 Steven G. Louie (Berkeley)

Ab Initio Optical Properties from the Bethe-Salpeter Equation: Atoms to Solids

10:15 Eric Shirley (NIST)

Optical properties: treating metals, strain, and non-zero q

11:00 Coffee Break

Chairperson: F. Bechstedt (Jena)

11:30 Michael Rohlfing (Münster)

Excitons and Optical Spectrum of the Si(111)-(2x1) Surface

12:15 Peter Bobbert (Eindhoven)

Electro-optical excitations in conjugated polymers

13:00 Lunch

Chairperson: E.K.U. Gross (Würzburg)

14:30 George F. Bertsch (Seattle)

Application of real-time TDLDA to optical response

15:15 James R. Chelikowsky (Minesota)

Predicting Excited State Properties in Clusters Using the Time Dependent Local Density Approximation in Real Space

16:00 Coffee Break

Chairperson: E. Shirley (NIST)

16:30 Xavier Gonze (Louvain)

Potential energy surfaces for excited states from Time-Dependent Density-Functional Theory

16:50 Pietro Ballone (Messina)

Simple approximations and computer experiments to evaluate electron excitation energies

17:35 ROUND TABLE: Round Table on TDDFT versus Green's Function methods (Coordinator: R. Resta)

18:35 End

20:00 Social Dinner

Friday 3 September

Chairperson: W. Eckardt (FHI, Berlin)

09:00 Xavier Gonze (Louvain)

Exchange and Correlation Kernels at the Resonance Frequency – Implications for Excitation Energies in Density-Functional Theory

09:45 Stan van Gisbergen (Amsterdam)

Analysis of linear term in xc potential of finite systems

10:30 Coffee Break

Chairperson: U. von Barth (Lund)

11:00 Raffaele Resta (Trieste)

Does the many-body Green's function provide the many-body Berry phase?

11:45 Hardy Gross (Würzburg)

Dichroism in the frequency-dependent response of superconductors

12:30 Jorge Pacheco (Coimbra)

Structural effects in the calculation of Electronic excitations in simple metal clusters

13:15 Lunch

14:00 ROUND TABLE: Continuation of the Round Table (Coordinator: R. Resta)

15:45 CONCLUDING REMARKS

16:00 Coffee Break

16.15 Meeting of the NANOPHASE groups (to discuss future activities etc)

18:00 End

Abstracts of Talks

Optical properties of large systems: Towards a many-body description

F. Bechstedt, W.G. Schmidt, B. Adolph, and J. Furthmueller
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Abstract

We present two examples for a reasonable description of optical properties of systems with extremely large unit cells. (i) The first example concerns polar InP and GaP(001)2x4 surfaces, which are represented by slabs containing more than 100 atoms. An approximate description of the self-energy and excitonic effects is combined with a real-space multigrid approach. (ii) In the framework of extremely softened non-normconserving Vanderbilt pseudopotentials we are able to treat supercells with at least 216 atoms. Unfortunately there are no complete wave functions. However, we show how momentum-matrix elements can be obtained within the projector augmented-wave method.

Application of real-time TDLDA to optical response.

K. Yabana,
Niigata University E-mail: yabana@carrot.sc.niigata-u.ac.jp
and
G.F. Bertsch, *University of Washington E-mail: bertsch@phys.washington.edu*

Abstract

We have been surveying the applicability of the time-dependent local density approximation as a theory of electronic excitations, calculating various clusters and molecules. The real-time method allows us to compute the entire response at once, which is advantageous in treating response in the UV domain. The systems we have considered are:

–large (N=100) alkali metal clusters [1]
–carbon chains (N=3-15) [2]
–conjugated carbon molecules(polyenes,benzene,retinal,C_{60}[3]
–silver clusters (N=2-8) [4]
–chiroptical response [5]

Our experience is that the TDLDA reproduces the strong transitions rather well, getting the frequencies to about 10% accuracy and the oscillator strengths to 25%. This is very encouraging to try to apply the TDLDA to more ambitious questions. Concerning the chiroptical response, the circular dichroism in the cases we studied is only reproduced to a factor of 3, and the low-frequency optical rotatory power seems beyond the accuracy of the TDLDA.

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[2] "", Z. Phys. D42 219 (1997).
[3] "", Int. Journ. Quantum Chemistry 75, in press; physics/9808015.
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Predicting Excited State Properties in Clusters Using the Time Dependent Local Density Approximation in Real Space*

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Abstract

Determining excited state properties of atomic clusters is a challenging problem for several reasons. In general, ground state structural properties are unknown and not subject to direct experimental probes. Without knowledge of the ground state structural properties, it is not possible to predict accurate excited state properties such as optical excitations. We present a *real space method* to determine the structural properties of semiconductor clusters and the corresponding optical properties. A combination of higher-order finite difference techniques and *ab initio* pseudopotentials constructed within density functional theory is used to compute *quantum* interatomic forces. These forces can be used to perform simulated annealing to determine the structural properties of clusters. Real space approaches have several advantages in this procedure. For example, the "basis" is unbiased, charged clusters can be easily accommodated and the algorithm is suitable for implementation on parallel platforms. Once the structural properties have been determined, we use the time dependent local density approximation (TDLDA) to extract the excited state properties of clusters. We demonstrate that TDLDA can yield accurate optical properties via a comparison to experiment. TDLDA is very efficient and easily added on top of electronic structure programs. Also, we will compare the results of TDLDA to other theoretical approaches such as solutions of the Bethe-Salpeter equations for confined systems.

I. Vasiliev, S. Öğüt and J.R. Chelikowsky, *Phys. Rev. Lett.* **78**, 4805 (1997); **82**, 1919 (1999).

* Supported by the National Science Foundation and the Minnesota Supercomputing Institute.

Calculated lifetimes of hot electrons in aluminium and the nobel metals using a plane wave basis set

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Abstract

We report about the lifetimes of hot electrons in crystalline Aluminum and in copper and Silver. For Aluminum the results agree quantitavely with the experimental data. For Cu we get good agreement for quasiparticle energies in the (110) direction above 2eV. For Ag the theoretical results are in good agreement with available experimental data for all energies [in (110) direction].
The calcultions were performed within the shielded interaction aproximation (SIA or GWA) using a plane wave basis set. We show that for Cu and Ag this basis leads to equally good results as the more demanding LAPW basis.

Improved Exchange and Correlation Energy Functionals

Paula Friera and Rex Godby
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Abstract

The current approximations for the exchange and correlation energy in Density-Functional Theory fail to describe many important aspects of some complex systems, such as the barrier heights of several chemical reactions (1). In Many-Body Theory, the exchange and correlation energy is treated from a fundamental point of view, using the self-energy operator Σ. However, calculating Σ for real materials is computationally very expensive and in many cases not feasible.

We propose a new method for calculating total energies of interacting systems, in which the self-energy operator is modelled in a simple way (2) that nevertheless retains the main features of the exact operator. The total energy is calculated by means of the Galitskii-Migdal total energy formula that appears in Many-Body Theory. In this way, the major part of the exchange and correlation energy is treated in a much more realistic way than in traditional density functional theories, while the small remaining part is approximated locally so that our approach is exact in the limit of homogenous densities. The method has been tested to calculate total energies of the imhomogenous electron gas and of bulk silicon.

[1] J.C Grossman and L. Mitas, PRL **79** 4353 (1997)

[2] R.W. Godby, M. Schluter and L.J. Sham, PRB **37** 10159 (1988)

Analysis of linear term in xc potential of finite systems

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Abstract

We recently found huge overestimations in LDA and GGA calculations on the (non)linear optical properties of finite molecular chains [1, 2]. Subsequent analysis showed this problem to be related to "Density-polarization functional theory" [3]. This extension of DFT for periodic systems has recently also been discussed by many other authors (Resta, Martin,

Ortiz, Souza, Vanderbilt). It was shown that a linear term can exist in the exchange-correlation (xc) potential for polarized systems.

We analyze the consequences for finite molecular chains of varying size, for which the xc functionals do not need to depend on the polarization. For this analysis we use both "exact" xc potentials and the x-only Krieger-Li-Iafrate (KLI) potential [3, 4]. The results show that the linear term in the xc potential counteracts the externally applied electric field, and has its origin in the so-called "response" part [5] of the xc potential, not in the well-known potential of the xc hole.

A close analysis of the KLI potential reveals the mechanism through which orbital-dependent functionals can generate such a counteracting term, thus providing the "ultra nonlocal density dependence" which is missing in LDA and GGA functionals (which lack the required linear term). Such understanding should be the first step towards improved xc functionals.

References:

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Exchange and Correlation Kernels at the Resonance Frequency – Implications for Excitation Energies in Density-Functional Theory

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Abstract

Specific matrix elements of exchange and correlation kernels in time-dependent density-functional theory are computed. The knowledge of these matrix elements not only constraints approximate time-dependent functionals, but also allows to link different practical approaches to excited states, either based on density-functional theory, or on many-body perturbation theory, despite the approximations that have been performed to derive them [published in Phys.Rev.Lett.**82**, 4416 (1999)].

Potential energy surfaces for excited states from Time-Dependent Density-Functional Theory

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Abstract

The usefulness of Time-Dependent Density Functional Theory (TD-DFT) for the computation of excitation energies of atoms, molecules and clusters, has been demonstrated recently [1-4]. Here this formalism is applied to the computation of excited state potential energy surfaces. For the $(\mathrm{HeH})^+$ system, we investigate the ground state as well as the 5 lower-lying singlet and triplet states, for a series of internuclear distances. We work both in the Local Density Approximation (TDLDA) and in the exchange-only Optimized Effective Potential approximation (TDOEP). For this system, comparison with Configuration Interaction (CI) data shows that TDLDA is insufficient. TDOEP gives much better results, especially for the position of the avoided crossings between the different curves. The good approximation to the exact exchange-correlation potential provided by the OEP partly explains this observation. Surprisingly, for some of the singlet excited states, the straight OEP Kohn-Sham eigenvalue differences, that constitute the starting point of TDOEP, are in even better agreement with CI data. We also compute excited state energies within the ΔSCF approach, using both LDA and GGA. In general, TDOEP and ΔSCF results show comparable accuracy.

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Dichroism in the frequency-dependent response of superconductors

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Abstract

How do excited electrons behave in superconductors? To investigate this question we study the phenomenon of dichroism, i.e., the fact that under certain circumstances the power absorption of left-handed circularly polarized light differs from the power absorption of right-handed circularly polarized light. In normalconducting metals dichroism is observed if a static magnetic field (either external or internal, due to ferromagnetic order) is present in addition to the external light source. Theoretical investigations have demonstrated that this phenomenon is a relativistic effect: Without spin-orbit coupling there is no dichroism in normalconducting metals.

To study dichroism in superconductors we therefore will first present a relativistic generalization of the Bogolubov-de Gennes equations where the particle and hole amplitudes are Dirac spinors [1,2]. In the weakly relativistic limit one obtains, besides the usual spin-orbit, Darwin and kinetic energy corrections, an additional “spin-orbit” and an additional

"Darwin" term [1,3]. The latter terms are present in superconductors only and involve the pairing field in place of the electrostatic potential. On the basis of these equations we then identify four distinct mechanisms for dichroism in superconductors [4,5]. Two are modifications of mechanisms known from the normal state, and two are novel mechanisms found in superconductors only. We solve the equations for a simple model superconductor and find a variety of new effects, not known from dichroism in the normal state.

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Equation: Atoms to Solids

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Abstract

In this talk, I will briefly review a first-principles approach [1,2] to the optical properties of materials based on making the GW approximation to the quasiparticle self energy and solving the two-particle Bethe-Salpeter equation for the optically excited states. In particular, we examine the validity of this approach to the optical absorption of various systems. In many cases, an accurate determination of the quasiparticle wavefunctions by solving fully the Dyson's equation is found to be necessary for accurate results. That is, the quasiparticle wavefunctions can be significantly different from the LDA or GGA Kohn-Sham eigenfunctions, and these differences can strongly affect the calculated quasiparticle energies, exciton energies, and optical spectra. We present results from calculations on atoms, clusters, and crystals. For atoms and small clusters, our results are compared with best available results from quantum chemistry methods including the quantum Monte Carlo method. As a specific example of crystals, we discuss our results for SiO2 and try to resolve some of the long-standing issues regarding the optical spectrum of this important insulator.

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Many body GW calculation of the total energy of electron systems

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Abstract

Hedin's *GW* approximation has been extensively used to calculate the one-electron excitation spectra of a wide variety of systems.[1]

However, there are not many results concerning the ground state properties, such density[2] or total energy[3, 4], obtained from the one-particle Green's function G which arises after a *GW* calculation.

Obviously, the main reason is the routine use of the Density Functional Theory (DFT) as a practical tool for such ground state calculations. However, the most popular implementations of the DFT (LDA or GGA) lack predictive accuracy in many cases.

An alternative approach to ground state calculations is based on many-body perturbation theory. In this context, Hedin's original *self-consistent GW* approximation can be viewed as a Φ-derivable model (in the Baym-Kadanoff sense). Hence, the *self-consistent* Green's function verifies exactly particle number and energy conservation laws.[4, 5]

In this work we present fully self-consistent *GW* results for simple electron systems (the homogeneous 2D and 3D electron gases, and jellium slabs), and the corresponding ground state properties. Note that whereas self-consistent *GW* calculations for inhomogeneous systems have been already performed,[6] these standard *GW* methods are not able to give a Green's function with the minimum level of accuracy to obtain meaningful ground state properties. Careful analysis of asymptotic behaviours of Green's function as well as the use of the space time method developed by Rojas *et al.*[7] allow us to obtain G with the desired precision.

References

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Developments and applications of the GW space-time method

L. Steinbeck[†] A. Rubio[‡], L. Reining[§], M. Torrent[§], I. D. White[+], and R. W. Godby[†]
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Cambridge, CB3 0HE, UK

Abstract

I shall describe recent developments of the space-time method [1,2], and applications including the quasiparticle band structure of gallium nitride.

1. "The GW space-time method for the self-energy of large systems", Martin M. Rieger, L. Steinbeck, I.D. White, H.N. Rojas and R.W. Godby, Computer Physics Communications **117** 211-228 (1999).
2. "Enhancements to the GW space-time method", L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I. D. White and R. W. Godby, submitted

Image Effects in Small Quantum Dots

Patrick Rinke and Rex Godby
University of York, UK

Abstract

Types of effects on excitation spectra that may be expected in GW calculations of realistic quantum dots are studied on a simple model quantum dot. In particular the impact of the electrostatic image potential and the centrifugal potential, arising in our spherical dots, are taken into account. The electron-electron interaction and the confining potential are replaced by a model potential and the material's properties are represented by their dielectric constants.

Three different changes have been observed. The potential and therefore the electron energies are shifted and the level spacing in the excitation spectrum changes. Additional one-electron energy levels occur and a continuum of infitesimally seperated levels establishes at the potential edge. An intrinsic barrier arises for angular momentum excitation that creates meta stable states. All of these changes become more visible with shrinking dot size.

Excitons and Optical Spectrum of the Si(111)-(2x1) Surface

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Abstract

We investigate excitons at the Si(111)-(2x1) surface and their optical spectrum from first principles. To this end, we first solve Dyson's equation for the one-particle Green's function, yielding the quasiparticle excitations of the system. The electronic self-energy operator is calculated within the GW approximation. Thereafter, we solve the Bethe-Salpeter equation for the two-particle Green's function of coupled electron-hole pairs, fully including the electron-hole interaction.

The optical spectrum of the Si(111)-(2x1) surface is dominated by a surface exciton formed from the pi-bonded surface states. The excitonic binding energy is more than one order of magnitude larger than in bulk Si. The two-particle wave function of the exciton state is strongly localized at the surface and exhibits distinct anisotropy due to the surface reconstruction.

Simple approximations and computer experiments to evaluate electron excitation energies

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Contrada Papardo 98166 Messina, Italy

Abstract

The talk will be divided into two parts. In the first part, I shall present a simple method for estimating electron removal energies from ground-state density functional computations [1]. Moreover, I shall discuss the relation of the proposed method with previous schemes, like the self-interaction correction, the Slater transition state method, and a semi-empirical scheme proposed by S. B. Trickey in 1986 [2]. The comparison of the results obtained with the new scheme with experimental data for atoms and molecules shows that the proposed method corrects most of the error present in the single electron eigenvalues of density functional theory.

In the second part of the talk, I shall discuss the advantages and limitations of quantum Monte Carlo methods in the evaluation of excitation energies, focusing mainly on collective excitations.

[1] M. Harris, and P. Ballone, Chem. Phys. Lett. **303**, 420 (1999)

[2] S. B. Trickey, Phys. Rev. Lett. **56**, 881 (1986).

Electro-optical excitations in conjugated polymers

J.-W. van der Horst,P.A. Bobbert, M.A.J. Michels,G. Brocks and P.J. Kelly
Eindhoven University of Technology, The Netherlands

Abstract

We calculate the one- and two-particle excitations in polythiophene by using the GW approximation and solving the Bethe-Salpeter equation, respectively. The screening of the Coulomb interaction plays a crucial role in both kinds of excitations. We study the effects of intra- and interchain screening separately. The first kind of screening is treated in an ab-initio manner. The second kind of screening is obtained from a model in which the polymer chains are treated as polarizable line objects. From this model we obtain the frequency-dependent dielectric tensor for an experimentally determined crystal structure, which is then used to describe the interchain screening. It turns out that the fundamental gap as well as the exciton binding energy are very much affected by the interchain screening. However, the optical gap, i.e. the difference of the two former quantities, is hardly affected. Only by including the interchain screening we obtain agreement with various electro-optical experiments. We expect our conclusions to be valid for conjugated polymers in general.

Electronic structure of II-VI semiconductors: HF, LDA, EXX and GW calculations

Andrzej Fleszar
Universität Würzburg, Germany

Abstract

I will review my calculations of the electronic structure of II-VI semiconductors, done with various methods. Because of an interplay of the localized semi-core states with the valence states in IIb-VI compounds, these materials play important role as a test case for theoretical approaches.

On correlation effects in x-ray absorption spectroscopy

Lars Hedin*,% , L. Campbell#, J. J. Rehr#, and W. Bardyszewski+
* *University of Lund Lund, Sweden*
% *Max Planck Institute for solid state research, Stuttgart, Germany*
#*University of Washington, Seattle, USA*
+ *Warsaw University, Warsaw, Poland*

Abstract

The one-electron spectral function is an important ingredient in all electron spectroscopies. It has a quasi-particle peak of strength Z(k), and a satellite structure of strength 1-Z(k), where k is the electron momentum. The function Z(k) is typically 0.6-0.8 for k smaller than the Fermi momentum kF. As shown by B. I. Lundqvist already in 1969 Z(k) has an anomalous behaviour and can drop to quite small values when k approaches kF+qc, where qc is the momentum where Landau damping of plasmons sets in. At larger k-values Z(k) slowly approaches 1. The effect of correlation on x-ray absorption is analyzed by using an expansion in fluctuation potentials as proposed by Bardyszewski and Hedin in 1987. We find strong interference effects for energies just above the Fermi energy, before the anomalous region is reached. For higher energies the intrinsic effects dominate, and the spectrum becomes a convolution of the core-electron spectrum and the usual one-electron expression, as predicted by Rehr and collaborators in 1978.

Structural effects in the calculation of Electronic excitations in simple metal clusters

Jorge Pacheco
University of Coimbra, Portugal

Abstract

The role of including explicitly the geometric structure in the calculation of the photoabsorption process in simple metal clusters is investigated. Quantitative agreement with recent low-temperature experiments on charged clusters is obtained by means of a simple theory in which the role played by the ionic skeleton becomes particularly transparent.

Does the many-body Green's function provide the many-body Berry phase?

Raffaele Resta
Dipartimento di Fisica Teorica, Università di Trieste, Italy

Abstract

The many–body Green's function embeds by construction the complete information about the (N+1)-particle and (N-1)-particle excitations of a given sistem: it also provides some partial information about the N-particle ground state. In particular, knowledge of the many-body Green's function is enough to recover the one-body reduced density matrix and the ground-state energy: other observables, like two-body (and higher order) correlation functions are instead not accessible.

Berry phases occur in many fields of physics: they are a kind of "exotic" observable, which cannot be cast as the expectation value of any operator, being instead a gauge-invariant phase of the wavefunction [1]. Here I focus on a generic Berry phase in a many-electron system: two simple examples are the Aharonov-Bohm phase [2], and the phase generated by a conical

intersection in a molecule [3]. In order to evaluate a Berry phase, one needs in principle the full N-body wavefunction: since many-particle wavefunctions are nasty objects, carrying redundant information, it is worthwhile to assess whether the many-body Berry phase can be expressed in terms of simpler quantities.

I start with the uncorrelated case, where the ground wavefunction is a determinant of single-particle orbitals: in this simple case, one can prove that the many-body Berry phase is just the sum of the individual Berry phases of each orbital [1]. Switching then the interaction on, the question is whether one may continue to express the many-body Berry phase in terms of the Feynman-Dyson amplitudes (despite the fact that the latter are not orthonormal). I conjecture that the answer is "yes". I will present a proof for the special case of the Aharonov-Bohm phase; the problems of a general proof will be outlined.

[1] R. Resta, "Berry Phase in Electronic Wavefunctions"; Lecture Notes for the Troisieme Cycle de la Physique en Suisse Romande (Lausanne, Switzerland 1996). Available online (194K) at the URL: http://www-dft.ts.infn.it/ resta/publ/notes_trois.ps.gz gzipped file

[2] R. P. Feynman, R. B. Leighton, and M. Sands, "The Feynman Lectures in Physics", Vol. 2 (Addison Wesley, Reading, 1964), Sect. 15-4.

[3] C.A. Mead, "The geometric phase in molecular systems", Rev. Mod. Phys. 64, 51 (1992).

Optical properties: treating metals, strain, and non-zero q.

Eric Shirley
NIST, USA

Abstract

This talk will focus on efforts to treat optical properties in metals in addition to insulators. Studying metals complicates matters because of the possibility of intra-band transitions. In addition, recent developments to treat non-zero momentum transfer will be discussed. These have permitted the interpretation of a wide variety of inelastic x-ray and electron scattering data.

Also, several algorithmic refinements have been made that better automate and make more efficient earlier work. These refinements have permitted more detailed zone sampling and extension of calculations to a greater number of conduction bands, which permits replication of experimental absorption features with remarkable fidelity and detail up to as far as 25 eV above the absorption edge (with inclusion of even more bands possibly permitting treatment of even wider spectral regions). With this, the goals of treating practical optical materials with more complicated crystal structures and of treating optical properties as a continuous function of strain have been considered.

Gradient expansion approximations to the kinetic energy functional

Ulf von Barth
University of Lund Lund, Sweden

Abstract

Many electronic-structure calculations in s-p bonded metals and in semi-conductors are carried out using pseudo-potentials and plane waves. In earlier work from 1995 we demonstrated that a straight- forward gradient expansion give exchange energies for the metallic pseudo systems that are accurate to within 1 mRy. There are reasons to believe that correlation energies can be obtained with similar accuracy from a new Meta-GGA by Perdew and coworkers. Unfortunately, the results for the s-p bonded semi-conductors are an order of magni- tude less accurate. This suggests two things: i) previous problems in obtaining accurate cohesive energies of s-p bonded metallic systems within DFT are mainly associated with the outskirts of the atoms, and ii) there is a definite problem with the GGA:s associated with the occurrence of a band-gap - an extremely non-local property. Recent investigations of the non-interacting kinetic energies of "pseudo" systems - perhaps the largest part of the total energies - again demonstrate the power of gradient expansions as long as exponentially decaying densities and band gaps are not considered. A solution to these two problems would open up the road to electronic structure calculations without the need for Schroedinger's equation.

Abstracts of Posters

Self-energy corrections in solids within a model GW scheme: electronic structure and effective charges in transition metal oxides.

S. Massidda[a], M. Posternak[b], A. Baldereschi[b,c] and R. Resta[c]
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[b] *Institut de Physique Appliquée, Ecole Polytechnique Fédérale,*
PHB Ecublens, CH-1015 Lausanne, Switzerland
[c] *Dipartimento di Fisica Teorica, Università di Trieste, I–34014 Trieste, Italy*

Abstract

The late transition–metal monoxides (MnO, FeO, CoO, NiO) have the rocksalt structure in their paramagnetic phase, while below the Neel temperature a weak structural distortion accompanies an AFM ordering of type II. Therefore, it is generally assumed that most *nonmagnetic* (*i.e.* spin–integrated) crystalline properties are essentially cubic: we give here convincing evidence of the contrary. We focus [1] on the half–filled *d* shell oxide MnO as the most suitable case study, on which we perform accurate ab–initio, all–electron calculations, within different one–particle schemes. In order to study the symmetry lowering due to AFM ordering, we assume an ideal cubic geometry throughout. The calculated TO frequencies and Born effective charge tensor do not have cubic symmetry. The standard LSD severely exaggerates the deviations from cubic symmetry, confirming its unreliability for calculating properties of insulating AFM oxides, while a model self–energy correction scheme [2] reduces considerably the anisotropy. We also explain the origin and the magnitude of this effect in terms of the mixed charge–transfer/Mott–Hubbard character of MnO.

[1] S. Massidda et al., Phys. Rev. Lett., **82**, 430 (1999). [2] S. Massidda *et al.*, Phys. Rev. B **55**, 13494 (1997).

Many-body effects on one-electron energies and wave functions: a study of the GaAs(110) surface

O. Pulci[1], F. Bechstedt[1], G. Onida[2], R. Del Sole[2], and L. Reining[3]
[1] *Friedrich-Schiller-Universitaet, Max-Wien-Platz 1, 07743 Jena Germany*
[2] *Università Tor Vergata, Rome, Italy*
[3] *LSI, Ecole Polytechnique, Palaiseau, France*

Abstract

We present a first-principles calculations for both the electron energies and the wave functions of a GaAs(110)1×1 surface within a nonperturbative quasiparticle approach. As a first step we solve the electronic-structure problem in the framework of the density functional theory (DFT) and the local density approximation (LDA). Using Hedin's GW scheme, in a second step the quasiparticle energies are calculated in first-order perturbation theory. In a third step, we determine the quasiparticle wave functions, written as linear combinations of the Kohn-Sham eigenstates, by taking into account nondiagonal components of the self-energy between DFT-LDA states.

The influence of the off-diagonal elements on the quasiparticle energies is almost negligible. Also the quasiparticle wave functions turn out to be in general quite similar to the DFT-LDA ones. However, for certain states we find a remarkable change of their localization behaviour as a consequence of the mixing between DFT-LDA states. As a sensitive observable for the effect of the difference between quasiparticle and Kohn-Sham wavefunctions, the reflectance anisotropy is studied.

Ab initio modelling of optical absorption on active sites in microporous silicates (zeolites)

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** The Royal Institution of Great Britain,*
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*** School of Engineering and Applied Science*
Dept chem Engineering, University of Virginia,
Thornton Hall, Charlottesville VA 22903-2442, USA

Abstract

Physical properties of catalytically active sites in zeolites have been intensively used in recent years to identify and characterise these species. Usual techniques including IR, solid-state NMR and EXAFS spectroscopies have heen recently complemented by optical studies in the UV/visible range [1]. This technique is particularly promising for transition metal centres and more generally Lewis and redox centres in assisting in a differentiation between the sites of different coordination and symmetry. Previous studies in this field [2,3] have shown that ab initio post-Hartree-Fock and Density Functional techniques have been very successful in the prediction of both the structures and ground state properties of these complex materials; modelling of excited states and optical transitions are now providing a new challenge to the ab initio study of zeolitic materials. A number of traditional methods including CIS, RPA and MRCI have been effective in dealing with similar problems for optical materials suggesting the application of these techniques will prove to be a fruitful approach to the study of the optical properties of zeolites. A new development in the time-dependent Density Functional theory as implemented in Gaussian98 and other codes provides us with the necessary means. We are particularly concerned with the optical spectra of the peroxide and Ti based active sites. Calculations are now in progress in which we investigate the shift in the absorption edge associated with a change in the coordination of Si atoms and possibly their oxidation (and therefore electronic) state. We also study the effect of water molecules coordinated to the Ti framework site on the optical properties. For this purpose we employ a molecular

cluster approach including the structural models derived previously [2] and refined for this study. The energy minimised structures (obtained from both periodic and molecular models) are being used for the optical calculations using TD DFT approach in the Gaussian98 code and calibrated against more computationally demanding post-Hartree-Fock techniques on smaller examples (1 T-site cluster). In particular, a singlet/triplet splitting in the electronic states of the 1T-site clusters of silica and tetrahedral Ti substitution is being calculated using both DFT and Coupled Cluster and MRCI methods.

1. Z.F. Liu and R.J. Davis. J. Phys. Chem. 98 (1994) 1253.
2. P.E. Sinclair et al. J. Phys. Chem. 101 (1997) 4232. P.E. Sinclair and C.R.A. Catlow J. Phys. Chem. B 103 (1999) 1084.
3. A.A. Sokol et al. In: Proc. 12 International Zeolite Conference, Ed. M.M.J. Treacy et al. Vol. 1, Baltimore, MRS 1998, 457. A.A. Sokol et al. J. Phys. Chem. B 102 (1998) 10647.

Organizing perturbation theory with trees

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Abstract

A method is presented to write the solution of equations involving functional derivatives as a recursive sum indexed by planar binary trees. The method is applied to quantum field theory. Each tree represents the sum of a number of Feynman diagrams. The formulas are explicit and the diagram multiplicities are generated automatically. The method is applied to the example of quantum electrodynamics.

Excitonic and quasiparticle gaps in Si nanocrystals

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Departement Institut Superieur d'Electronique du Nord
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Abstract

We present calculations of the one and two particle excitations in silicon nanocrystallites. The one-particle properties are handled in the GW approximation while the magnitude of the electron-hole interaction is obtained from the solutions of the corresponding Bethe-Salpeter equation. We develop a simplified tight-binding version of these methods allowing us to treat large clusters (up to 200 atoms) which cannot be treated by ab-initio methods. We show that the self energy and Coulomb corrections obey simple physical laws and almost exactly cancel each other for crystallites with radius larger than 0.6 nm. The result of this

cancellation is that simple one-particle calculations (corrected LDA, empirical tight-binding or pseudopotentials) give quite accurate values for the excitonic gap of crystallites in the most studied range of sizes.

Density functional calculations of the adiabatic surfaces of the lowest excite states in crystalline NaCl

J. L. Gavartin and A.L. Shluger
Condensed Matter and Materials Physics,
Department of Physics and Astronomy, University College London,
Gower Street, London WC1E 6BT, U.K

Abstract

The triplet self-trapped excitons (STE) in alkali-halide crystals are the prototype systems for studies of exciton self-trapping phenomena in insulators. Despite being a subject of intense experimental and theoretical studies, many features of the STE structure and dynamics remain unclear. Previous first principles calculations of the STE suffered from small model systems, restricted basis sets, and little or no account of electron correlation. These limitations can be partially lifted by the use of the plane wave spin polarised density functional techniques implemented on massively parallel computers. We present the first such calculations of the STE in NaCl which were performed using the VASP code [1], implementing the gradient corrected density functional with non-local pseudo-potential. The adiabatic potential energy surfaces and charge/spin densities of the crystal in the singlet and triplet states (which are the lowest energy states for the corresponding total spin quantum numbers) were calculated within the periodic cells of up to 72 NaCl molecules. Based of this results we predict the photoluminescence energies as well as frequencies of certain local vibrational modes. We discuss the convergence of the results for different multiplets with respect to a cell size and a Brillouin zone mesh.

We also analyse the role of the correlation effects in the STE dynamics and discuss the applicability of the method to the studies of localised electronic excitations.

1. G. Kresse and J. Hafner, Phys. Rev. B 47, RC558 (1993)
2. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169, (1996)

Parallel algorithms for the calculation of electronic excitations

Gian-Marco Rignanese, S.G Louie, A. Canning and X. Blase
Departement of Physics, University of California at Berkeley,
and Materials Sciences Division, Lawrence Berkeley Laboratory,
Berkeley, CA-94720

Abstract

We discuss the parallelization of the algorithms used to compute the quasiparticle energies within the GW approximation and to calculate the optical excitations by solving the

Bethe-Salpeter equation (BSE) to include excitonic effects. For several stages of the GW calculation, including the calculation of the RPA polarization, static dielectric matrix, and self-energy operator, the most efficient parallel scheme consists simply in distributing the conduction bands between the processors. Since the number of conduction bands required for an actual calculation can be quite large (typically 5-10 times the number of valence bands), this scheme is suitable and quite efficient for most finite and infinite-periodic systems. For the calculation of optical excitations, this simple and natural distribution is no more possible since the number of conduction bands needed in the Bethe-Salpeter matrix can be very small. Therefore, for the implemetation of the BSE, we develop a scheme different from that used in the GW calculation. For all these algorithms, we discuss the load balancing, scalability, memory distribution, minimization of the I/O, as well as other technical issues. Further developments and possible improvements of the programs are proposed. Finally, we present some recent applications.

Lifetimes of excited electrons in NFE and noble metals

W.-D. Schoene, R. Keyling, W. Ekardt
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Abstract

We present results for the lifetimes of excited (so-called "hot") electrons in infinite, periodic systems. The lifetimes are obtained by evaluating the one-electron Green's function within the GW approximation. From the width of the quasiparticle peak in the retarded Green's function the lifetime of the corresponding state is determined. We apply our method to the nearly free electron (NFE) metal Al and the noble metals Cu, Ag, and Au. Our theoretical results are compared to experimentally obtained lifetimes. In Al the agreement is very good. We are even able to identify the states (wave vector and band) of the hot electrons which lifetime were probed in the experimental work using a polycrystalline sample. The experiments on the noble metals were performed wave vector resolved so that we can compare our results with the experimental data in the (110) direction. The agreement is good. However, we find that the GW approximation is unable to explain the sharp increase of the lifetime of excited electrons in Cu and Au for energies smaller than 2 eV. We also discuss some open questions and give an outlook to future work. The poster concentrates on the technical details of our calculation and complements W. Ekardt's talk.

5.3 Reports on Collaborative Visits

Report on a Collaborative Visit of T. Korhonen, (Laboratory of Physics, Helsinki University of Technology) to the Institut für Festkörperforschung, Forschungszentrum Jülich

30 August – 6 September 1999

From 30th August to 6th September 1999, I visited Dr. Stefan Blügel and his group at the Institut für Festkörperforschung in Forschungszentrum Jülich. The aim of my visit was to fetch the Jülich FLAPW code and to get some training on it and to discuss about the FLAPW method in general.

I have started to study Pd surfaces connected to a catalysis project going on here in Helsinki University of Technology. The aim is to study these systems using different theoretical methods, like first-principles calculations, EAM simulations, Monte Carlo simulations, etc. The main purpose of this work is to study the reactivity of alloy surfaces, in order to find better catalytic materials. Stefan Blügel's group has used the FLAPW code 'FLEUR' developed at FZ-Jülich extensively to study surfaces, adatoms on surfaces, surface alloys, and magnetism, so this method seems to be ideally suited for my needs.

The visit was very successful, and I imported the Jülich FLAPW code 'Fleur' here in Finland without any problems, because I got nice 'hands-on' training during my stay in Jülich. I am very grateful to the network for its support, which made my trip to Jülich possible.

Timo Korhonen

Report on a visit of Elwira Wachowicz (Wrocław, Poland) in Fritz-Haber-Institut, MPG, Berlin

12 July–30 August, 1999

I visited Professor Matthias Scheffler's group in Theory Department in Fritz-Haber-Institute, Berlin to calculate properties of Be(0001) and Mg(0001) surfaces as well as to discuss problems connected to such calculations. All the results were obtained with `fhi98md` code developed in Professor Matthias Scheffler's group using *ab initio* pseudpotential method.

During my staying in Berlin I was performing calculations for both surfaces within local density (LDA) and general gradient approximation (GGA) to the exchange-correlation energy. I calculated relaxations of 2/3 upper layers for (0001) slabs of different thickness and then I looked at the electronic properties of the relaxed systems. The results were obtained for various sets of input parameters including variety of special k points sets and cut-off energies. First look at them showed a suprisingly big differences between relaxation values calculated for Mg surface within LDA and GGA approximation which require explanation and further calculations.

Apart from calculations I had a chance to discuss problems appearing while calculating total energy using DFT pseudopotential method for metals. I presented my results and energy convergency problems on "official coffee talk" which helped me to deal with my problems and to reveal errors in the version of programme I had used.

Moreover talking to people experienced in such type of calculation who used the same code I learnt about practical aspects of using different types of exchange-correlation energy approximations as well as of methods of testing them. Very usefull and meaningfull were remarks and hints concerning the technique of performing the calculations.

I would like to add that because of the visit I am still allowed to use CPU time of computers belonging to Theory Department of Fritz-Haber-Institute, Berlin.

Finally I would like to admit that all the results will be included in my Ph. D. thesis.

Elwira Wachowicz

Report on a collaboraive visit of A. Taga (Uppsala University) to Prof. C.Ambrosch-Draxl's group (Karl-Franzens Univ. Graz)

October 4-12, 1999

My recent visit to Prof. C. Ambrosch-Draxl's group is a part of a longer term collaboration having the goal of calculating electron-phonon coupling for a variety of materials.

During my first visit in February (supported by the TMR network within the LAPW node), we started implementing a method for calculating electron-phonon coupling using the WIEN97 LAPW code. Although this scheme now works, since it is based on supercell calculations, it is very computer time consuming and impractical for use in complex materials. Recently, a linear response code has been developed in Prof. C.Ambrosch-Draxl's group, which if applied to electron-phonon calculation has great advantages over the supercell method.

The motivation for the present visit was to adapt the new code for calculating electron-phonon coupling constants. During my short stay, I have learned to use the code and we have performed the first tests for zone boundary phonons by comparing the results with supercell calculations. Furhter test for arbitrary phonons will soon follow. I have also got a good introduction to the self-consistent linear response formalism. Further, we discussed future applications of the method.

Adrian Taga

Uppsala University, October 20, 1999

Report on a Collaborative Visit of R. Grohmann (Institute for Physical Chemistry, University of Vienna) to the Institute for Solid State Research, Forschungszentrum Jülich

22 - 28 August 1999

From 18 to 28 of August 1999 I visited Stefan Blügel and his group at the Institut für Festkörperforschung in Jülich. The aim of my visit was to get acquainted with the local orbital extension to the FLEUR-package.

The groups in Jülich and Vienna have been collaborating in the past in the development of the FLEUR-package. This program applies the full potential linearized augmented plane wave formalism.

In particular, we have been working on an *ab-initio* calculation of CeO_2. In order to overcome the difficulties in describing the semicore states properly we applied the local orbital extension. Using this technique, the basis set of the calculation is enlarged only by the wavefunctions for local orbitals, which describe electronic states completely localized inside the muffin-tin spheres. The advantage of this technique is the small increase in basis functions, compared to a calculation in which the semicore states are treated in a separate energy window.

My visit in Jülich gave me the opportunity to discuss the application of the local orbitals to our calculations as well as the theoretical background with P. Kurz and G. Bihlmayer, who have done the implementation into the FLEUR-package. Furthermore I was introduced to other new capabilities of the latest version of the program, such as the application of spin-orbit coupling to the calculation.

Rainer Grohmann

6 News from CCP9

UK's Collaborative Computational Project 9 on "Computational Studies of the Electronic Structure of Solids"

6.1 Report on KKR Mini-Workshop

Daresbury (UK), November 17, 1999

Programme

11:00 - 12:00 *G.M. Stocks* (ORNL): "Recent Developments"

12:00 - 13:00 *H. Winter* (Karlsruhe and Daresbury): "Beginners Experience with Screened KKR and Questions to Experts"

13:00 - 14:00 *Lunch*

14:00 - 14:30 *J. Schwitalla* (Bristol): "Bloch Walls"

14:30 - 15:00 *M. Eisenbach* (Bristol): "Nanowires"

15:00 - 15:30 *L. Petit* (Aarhus): "Determination of Magnetostriction of Transition Metals in Real Space"

15:30 - 16:00 *R. Tyer* (Sheffield): "SIC-LSD calculations for Manganites"

Participants:

Eero Arola (Keele),Simon Crampin (Bath), Markus Eisenbach (Bristol), Arthur Ernst (Halle), Iosif Galanakis (Strasbourg), Nektarios Lathiotakis (Bristol), Martin Lueders (Daresbury), A. Moss (Warwick), Leon Petit (Aarhus), S.S.A. Razee (Warwick), Malcolm Stocks (ORNL), Dzidka Szotek (Daresbury), Juergen Schwitalla (Bristol), Paul Strange (Keele), Walter Temmerman (Daresbury), Gerrit van der Laan (Daresbury), Christine Vrettea (Keele), Hermann Winter (Karlsruhe and Daresbury), Matthew Woods (Keele)

This workshop was mainly reviewing recent experiences and applications of the screened KKR. In particular Malcolm Stocks (ORNL) and Hermann Winter (Karlsruhe and Daresbury) discussed the convergence of the screened KKR with respect to angular momentum and height of the screening potential. Attention was also given to optimize the calculation of the density of states through either analytical continuation from the complex energy plane or optimization of the determination of the zeroes of the screened KKR determinant. Applications focussed on studies of non-collinear magnetism (Malcolm Stocks), nanowires (Markus Eisenbach), calculation of Bloch Wall thickness (Juergen Schwitalla), anisotropy of orbital moments and magnetocrystalline anisotropy (Leon Petit). Finally, Rik Tyer (Sheffield) presented some recent results of the application of the SIC-LSD to the manganites $CaMnO_3$ and $LaMnO_3$.

6.2 CCP9 Workshop

Daresbury, 13 January 2000

The purpose of this workshop is to publicize CCP9's major projects at the time of the submission of its renewal proposal. Talks will be presented on the GW, the new flagship project, and on Bloch Walls, which covers results of the old flagship project. The remainder of the talks will cover other major projects such as Bond Order Potentials (BOP) and Car-Parinello (CP) which were past flagship projects. Two major new projects were instigated: the Order (N) and transport in mesoscopic systems and hybrid nanostructures.

10:30 - 11:00	Coffee
11:00 - 11:30	GW (Rex Godby, York)
11:30 - 12:00	Bloch Walls (Balazs Gyorffy, Bristol)
12:00 - 12:30	BOP (David Pettifor, Oxford)
12:30 - 13:00	QMC (Matthew Foulkes, Imperial College)
13:00 - 14:00	Lunch
14:00 - 14:30	Quantum Mechanical Modelling of Covalently Bonded Materials (R. Jones, Exeter)
14:30 - 15:00	SIC-LSD (Walter Temmerman, Daresbury)
15:00 - 15:30	BdG (Dzidka Szotek, Daresbury)
15:30 - 16:00	CP (Mike Payne, Cambridge)
16:00 - 16:30	Coffee
16:30 - 17:00	O(N) (Mike Gillan, University College London)
17:00 - 17:30	Transport (Colin Lambert, Lancaster)
19:00	Dinner

Registration is free but required by e-mailing w.m.temmerman@dl.ac.uk. Travel costs can be reimbursed for UK based participants.

The workshop's web page is: http://psi-k.dl.ac.uk/ccp9/ccp9-workshop.html

7 General Workshop/Conference Announcements

7.1 Mini-colloquium

on "Recent Advances in Computational Material Science"

Organized by: **W. Andreoni, B. Lundqvist and P. Ballone**

within the

18th General Conference of the Condensed Matter Division of the European Physical Society

Montreux, Switzerland, 13-17 March 2000

jointly with the Japanese Physical Society and the Swiss Physical Society

This mini-colloquium is devoted to advanced computational approaches to the science of materials. This will include both new promising methods and new applications that have marked progress in selected frontier areas of research. The focus will be on ab-initio approaches, with emphasis on recent implementations of density-functional-theory. Relevant applications using semi-empirical methods and classical potentials simulations will also be represented. Applications will include organic electronics and metal alloys, nanostructures and biological systems. Simulations of surface processes, and calculations of electronic as well as mechanical properties will be discussed.

It is expected that this mini-colloquium will be of interest to a significant fraction of the Psi-k community, having density functional methods and applications as one of its central topics.

More information is available at: http://www.eps-cmd18.ch

7.2 ChiPPS 2000

Second International Workshop on Challenges in Predictive Process Simulation
Wandlitz, Germany, 15-18 May 2000
http://www.ihp-ffo.de/chipps/00/Welcome.html

SECOND ANNOUNCEMENT AND CALL FOR PAPERS

Reply with subject "ChiPPS inform" to receive regular posting.

Reply with subject "ChiPPS remove" to receive no more posting.

ChiPPS is a series of interdisciplinary meetings aimed to bring together experts from three distinct fields:

- fundamental materials science,
- development of process simulation tools,
- manufacture of microelectronic devices.

In particular, it serves as a bridge between those who study physical properties at the atomic scale and those who simulate technological processing steps at the macroscopic level.

The purpose of ChiPPS is to identify current and anticipated challenges in process simulation for microchip technology from the point of view of technologists, programmers, and physicists. It is a "call for action" meeting, meant to stimulate a new wave of research relevant to process simulation by clarifying the needs and pointing out advantages and deficiencies in the existing theoretical and experimental approaches. A review paper summarizing ChiPPS'97 can be downloaded from
http://www.ihp-ffo.de/chipps/97/Ddoc/dpg.html

ChiPPS'2000 will be held in Wandlitz near Berlin, Germany, from 15 to 18 May 2000. Papers are solicited on subjects covering semiconductor physics and technology, such as:

- Diffusion in solids;
- Carrier transport in nanostructures;
- Deposition of dielectrics and metals;
- Epitaxial growth of semiconductors;
- Formation of silicide films;
- Reliability of dielectrics and interconnects;
- New materials for microelectronics;

- New concepts for microelectronic devices.

For more details, please see the Call for Papers posted at:
http://www.ihp-ffo.de/chipps/00/Welcome.html

7.3 ISLI 2000 Conference

Ions in solids and liquids and at interfaces

Florence Boot Hall, The University of Nottingham

Wednesday 5th - Thursday 6th January, 2000

Scope of the conference

Last call for participants: ISLI 2000

Contributed talks and posters are requested for the ISLI 2000 conference in Nottingham on 5th-6th January. This is a workshop style conference at which PhD students are particularly encouraged to attend and present their work. Please return the registration form by December 8th to Dr. Richard Wheatley. We look forward to seeing you in Nottingham!

Richard Wheatley and John Harding.

Computational and experimental studies of ions, including solid and liquid ionic substances, ions in solution, ions at interfaces (including grain boundaries, solid/liquid and solid/vapour interfaces), and adsorption on ionic crystals.

This will be a 'workshop' style conference in which the emphasis will be on presenting and discussing new applications, new techniques and new problems, rather than a 'showcase' of published work.

The conference will begin with lunch on Wednesday, 5th January, and finish at lunchtime on Thursday. There will be a poster session (with drinks) on Wednesday evening.

Contributed talks and posters are welcomed. Please send a title and brief abstract to one of the organisers. In keeping with the workshop style of the conference, abstracts will not be published.

The Nottingham University campus is situated in parkland about 4 km west of the city centre, alongside the main A52 road, which leaves the M1 motorway at junction 25. Good public transport is also available, and East Midlands airport is only 40 minutes away by road.

Support

The Royal Society of Chemistry, Statistical Mechanics and Thermodynamics Group (SMTG)

Collaborative Computational Project 5 on Computer Simulation of Condensed Phases (CCP5)

Organisers

SMTG and local organiser:

Richard Wheatley, School of Chemistry, University of Nottingham,

Nottingham NG7 2RD, UK.
E-mail Richard.Wheatley@nottingham.ac.uk. Tel: +44(0)115-95-13454,
Fax: +44(0)115-95-13562.

CCP5 organiser:

John Harding, Department of Physics, University College London,
Gower Street, London WC1E 6BT.
E-mail J.Harding@ucl.ac.uk. Tel: +44(0)171-419-3506,
Fax: +44(0)171-391-1360.

Registration

Please complete the registration form and send it, with a cheque in pounds sterling (payable to The University of Nottingham), to Dr. Richard Wheatley at the address above. Please state if an invoice is required. Rates for additional accommodation/meals are available on request.

Programme

Wednesday 5th January

13.00 Lunch and registration at Florence Boot Hall.

14.00 Interfaces.

Invited speaker: JIM RUSTAD, Pacific Northwest National Laboratory. ‘Molecular Simulation of Chemical Processes at Mineral-Water Interfaces’

15.30 Tea

16.00 Ions in solution.

Invited speaker: MICHIEL SPRIK, University of Cambridge.Title to be announced

19.30 Dinner.

21.00 Poster session. (Wine and soft drinks provided; bar is adjacent!)

Thursday 6th January

9.00 Ionic solids.

Invited speaker: PATRICK FOWLER, University of Exeter.Title to be announced

11.00 Coffee

11.30 Ionic liquids.

Invited speaker: MARK WILSON, University of Oxford.‘Networks, Chains, Rings and Holes: Intermediate-range order in ionic systems’

13.00 Close of conference. Lunch is available if required.

Ions in solids and liquids and at interfaces (ISLI 2000)

Florence Boot Hall, The University of Nottingham. 5th-6th January, 2000.

Registration form

Title .... Initials ...... Surname ....

Male or Female? ....

Address ....

....

....

....

....

Telephone .... Fax ....

E-mail address ....

Any special requirements (e.g. vegetarian) ....

Conference Costs in pounds sterling (sorry, no credit cards)

Conference Fee, including lunch and dinner on Wednesday 5th January

Full 45.00

RSC or SMTG member 35.00 ....

Student 25.00

Accommodation for Wednesday night and breakfast

on Thursday 6th January 30.00 ....

Lunch on Thursday 6th January 12.00 ....

Late registration (after 8th December 1999) 15.00 ....

TOTAL ....

8 General Job Announcements

Ab initio Theory of Photochemistry
(2 Post-doctoral and 2 Ph.D. Positions)

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin (Germany)

Photochemistry represents a rapidly growing, interdisciplinary field that aims at developing techniques for the external control of reaction dynamics through photon irradiation. A particularly high potential for future applications lies in reactions between molecules and surfaces, such as laser-induced desorption, which promises to soon become an efficient method for preparing surface microstructures as well as quantum-state selected molecules in the gas phase. While experimental techniques are now very refined, the formulation of a predictive theory still remains a challenge, however.

The Theory Department of the Fritz-Haber-Institut, as a co-initiator of the Priority Programme *Dynamics of Electron Transfer Processes at Surfaces* of the Deutsche Forschungsgemeinschaft as well as the European Research Training Network *Nanophase Photon Absorption and Spectroscopy with Electrons*, now invites applications for **Post-doctoral and Ph.D. Positions** in order to extend its activities in the field of photochemistry. The positions are available immediately, but starting dates until June 2000 are negotiable. One post-doctoral position, funded by the European Research Training Network, is reserved for a citizen of the European Union or an Associated State (Iceland, Israel, Liechtenstein, Norway) up to 35 years of age, excluding German citizens or long-term residents.

The principal goal of this project is to develop a quantitave description of laser-induced desorption together with tools for *ab initio* simulations of such processes. To this end, density-functional theory and many-body perturbation theory, centred around the GW approximation for the electronic self-energy, will be employed to calculate potential-energy surfaces for the ground state and excited transition states. Molecular-dynamics and wave-packet methods serve to analyse the reaction dynamics. A strong background in computational physics and experience with some of the above-mentioned techniques will hence be an advantage.

Applications and informal inquiries should be addressed to:

Dr. Arno Schindlmayr
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, 14195 Berlin, Germany
E-mail: schindlmayr@fhi-berlin.mpg.de
Tel. : +49 (0)30 8413-4817, Fax : +49 (0)30 8413-4701

Further information about the group is available at: http://www.fhi-berlin.mpg.de/th/th.html .

POSTDOCTORAL POSITIONS

Technical University of Denmark, Lyngby

Atomic scale simulations of materials, surfaces and biomolecules

Two postdoctoral positions will be available at the Center for Atomic-scale Materials Physics (CAMP) at the Technical University of Denmark from winter/spring 2000 or later. One position is in the area of atomic scale simulations of materials processes using molecular dynamics and density functional methods. The other position is in the area of density functional calculations and modeling of surface chemical and enzymatic processes. More information about the center can be found at:
http://www.fysik.dtu.dk

The positions are for two years, and the monthly salary is in the range dkr 23.500 - dkr 25.500 (USD 3600-3900) depending upon qualifications.

Further questions can be addressed to:
Professor Jens K. Nrskov (norskov@fysik.dtu.dk) or
Professor Karsten W. Jacobsen (kwj@fysik.dtu.dk).

Applications including a CV, publication list, and names of three references should be sent as soon as possible to:

Helle Wellejus,
CAMP, Department of Physics, DTU,
Building 307, DK-2800 Kongens Lyngby, Denmark
e-mail: helle@fysik.dtu.dk

POSTDOCTORAL POSITION

Institute of Materials Science (CSIC)
Barcelona, Spain

A postdoctoral position in the group of Dr. Pablo Ordejon at the Institute of Materials Science of Barcelona (Spain) is available, starting February 2000.

The research will be mainly focused on the theoretical modeling of the properties of carbon nanotubes, including electronic transport, growth, interaction with surfaces, metallic contacts and chemical species, etc. It will be developed within a European Union - funded RTD (Research and Technological Development) project, in which the group in Barcelona will provide theoretical support to the experimental and industrial partners. Strong interaction with the other groups is therefore expected.

The successful candidate should have a PhD in Physics, Chemistry or Materials Science, and have an ongoing interest on nanoscale materials. Preference will be given to candidates with strong background in any (or several) of these fields: electronic transport in nanoscale systems, electronic structure calculations, molecular dynamics, and modeling of STM.

The position is for one year, with the possibility of renewal for up to three years upon mutual agreement. Some preference will be given to candidates from any of the countries of the European Union, although other nationalities will be given full consideration. The salary will be set according to the CSIC rules, depending on experience and qualifications.

Interested candidates should send immediately a CV, list of publications, and name and address (including email) of three references, preferably by email or fax, to:

Dr. Pablo Ordejon
Institut de Ciencia de Materials de Barcelona - CSIC
Campus de la UAB
08193 Bellaterra, Barcelona (SPAIN)

email: ordejon@pcd34a.icmab.es
fax: 34 93 5805927
phone: 34 93 5801853

Post-Doctoral Positions in Electronic Structure Theory National Renewable Energy Laboratory (NREL)

http://www.sst.nrel.gov

NREL's Solid State Theory Group is looking to fill two post-doctoral/research associate positions in the area of Electronic Structure Theory. The positions are for 2-3 years. The salary range is $44,000-$53,000/year, depending on qualifications and rank. One position is in the area of semiconductor physics, available immediately, and the second position is in the area of alloy electronic structure theory, to start summer or fall 2000. Applicants are expected to have a background in solid-state theory. Applications for both positions are considered now.

The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory (see an online list of current and past personnel in the group) and interacts with a broad range of experimentalists. Furthermore, the group has outstanding computational facilities: a dedicated local computing system consisting of a 16 node SGI Origin 2000 and 10 IBM RISC machines, and remote access to a Cray T3E and C90. The group has an excellent basic-research atmosphere, and is located in the beautiful Rocky Mountains. Consult our web page for additional information on the group, its history, research subjects, publications, and facilities.

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

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

NREL is an equal opportunity/affirmative action employer. Clarification or further details can be obtained via e-mail to azunger@nrel.gov.

Postdoctoral Research Position in Computational Defect Physics

We at the National Renewable Energy Laboratory (one of the DOE's prestige National Laboratories) invite applications for a postdoctoral research position, available immediately. This position is for two years, renewable upon mutual agreement to a third year. The research objective is to study defect-related doping properties of semiconductors and insulators and to come up with new design principles in order to overcome existing doping bottlenecks: An exciting field that may enable new technologies both in photovoltaic and IC applications. The starting salary is US$40-50 K/year depending on qualification. NREL is located near the beautiful Rocky Mountains, a gate to the wild west and ski resorts. There are currently about ten Ph. D.'s at NREL working in condensed matter theory. We have outstanding computational facilities, excellent basic-research atmosphere, and interact with a broad range of experimentalists at NREL. Candidate should send a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to

Dr. Shengbai Zhang
Computational Materials Science Group
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401, USA

NREL is an equal opportunity/affirmative action employer. Clarifications or further details can be obtained via e-mail to: szhang@nrel.gov

Postdoctoral Position
Department of Physics, University of California at Davis

A postdoctoral position working with the group of Warren Pickett in the condensed matter theory group at UC Davis is available immediately. Research areas include studies of the superconducting and magnetic behavior in complex compounds, and the study of superconductivity in a magnetic background. Development of novel electronic techniques to address both structural complexity and strong interactions will be an integral part of the research. Experience in the development and use of electronic structure techniques using density functional methods, or of Ginzburg-Landau or quasiclassical Green's functions is desirable. Experience with linux computer systems may also be a consideration. The position is expected to be available for up to two years. UC-Davis provides a competitive salary and benefits.

Please send a copy of your curriculum vitae, a description of your research experience, and the names and addresses of three references.

Prof. Warren E. Pickett
Department of Physics
University of California
One Shields Avenue
Davis CA 95616-8677

Phone: (530) 752-0926
Fax: (530) 752-4717
Email: pickett@physics.ucdavis.edu

Home page: http://yclept.ucdavis.edu/wep.html

Postdoctoral Research Fellow Positions in Electronic Structure Theory and Quantum Electronic Transport

National Microelectronics Research Centre (NMRC), Ireland

The Computational Modelling Group at the National Microelectronics Research Centre (NMRC), Ireland has openings for postdoctoral research fellows in the areas of electronic structure theory and quantum electronic transport.

The NMRC is Ireland's largest research centre and currently employs 260 people. There are fabrication facilities for silicon and compound semiconductor processing and a new national initiative on nanotechnology is underway at the centre. Details are at http://nmrc.ucc.ie

The Computational Modelling Group is a multi-disciplinary effort which is applying a multi-scale simulation approach to problems in microsystems, nanoelectronics and molecular electronics. The group is participating in the European Union's Future & Emerging Technologies research initiative in the areas of nanotechnology information devices and quantum information processing and communication.

We are seeking highly qualified individuals with an interest in applying electronic structure theory to problems related to point defects and zero-dimensional structures, molecular charge transport and heterostructure engineering. A variety of projects exist and interested candidates are encouraged to contact:

Dr. Jim Greer, Group Director - Modelling
NMRC, Lee Maltings, Prospect Row, Cork, Ireland
Tel: +353 21 904305
Fax: +353 21 270271
e-mail:jgreer@nmrc.ucc.ie

or to make a formal application to

Mr. Cormac Harrington, Administration Manager
NMRC, Lee Maltings, Prospect Row, Cork, Ireland
Tel: +353-21-904232
Fax: +353-21-904058
email: careers@nmrc.ucc.ie

Postdoctoral Research Position
Department of Physics, University of Padua, Italy

We invite applications for a post-doc position, available soon in our group (Condensed Matter sector (INFM), Department of Physics at the University of Padua, Italy). The successful candidate is expected to have experience in ab initio techniques and his/her research project will mainly concern first principles applications to transition-metal clusters.

The duration of the position is 2 years and the salary will be 30000000 ITL (25000000 ITL for an Italian).

For further information please contact:

Prof. F. Toigo
Istituto Nazionale per la Fisica della Materia and
Dipartimento di Fisica G. Galilei
Via Marzolo 8
I-35131 Padova, Italy
fax +39-049-8277102
tel. +39-049-8277170
e-mail: toigo@padova.infn.it

Ph. D. Studentship

Condensed Matter and Materials Physics
Physics and Astronomy Department, University College London, UK

A studentship is available immediately to support a three-year programme of work leading to a Ph.D. in the Condensed Matter and Materials Physics area (CMMP) in the Physics and Astronomy Department at University College London.

Established in 1994, CMMP has expanded rapidly, and now has roughly 50 members, including about 20 Ph.D. students. The CMMP area consists of both experimentalists and theorists, who have very wide-ranging interests, going all the way from the physics of high-pressure ice to the properties of novel magnetic materials, and from the temperature in the Earth's core to atomic-scale microscopy. This all makes CMMP one of the most exciting and stimulating places in the UK for doing a Ph.D. in condensed-matter physics.

Physics and Astronomy at UCL is one of the leading departments in the UK, with a strong commitment to excellence in both research and teaching. In the 1996 national Research Assessment Exercise, the Department was awarded a grade 5A, a result bettered only by two other departments in the UK.

The Ph.D. studentship available now is not tied to any particular research project, and could be used to support work in any of the many experimental and theoretical projects being done in CMMP. If you are interested and would like to know more, please send an e-mail to Professor Mike Gillan (m.gillan@ucl.ac.uk), who will be delighted to send you further information.

To find out more about the work of CMMP, the Physics and Astronomy Department, and UCL in general, please take a look at the following web pages:

CMMP: http://www.cmmp.ucl.ac.uk
Physics and Astronomy: http://www.phys.ucl.ac.uk
UCL: http://www.ucl.ac.uk

9 Abstracts

STM-Images of transition-metal structures buried below noble-metal surfaces

S. Heinze[1,2], R. Abt[1], S. Blügel[1], G. Gilarowski[3], and H. Niehus[3]
[1] *Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany
[2] *Zentrum für Mikrostrukturforschung, Universität Hamburg,*
D–20355 Hamburg, Germany
[3] *Institut für Physik, Oberflächenphysik und Atomstoßprozesse,*
Humboldt–Universität zu Berlin, D–10115 Berlin, Germany

Abstract

We analyse scanning tunneling microscopy (STM) experiments of Ir impurities and chains buried in the sub-surface layer of Cu(001) by first-principles calculations based on the density-functional theory and show for the first time that metal atom defect structures below a metal surface can be detected by STM. We show that this is not particular to the Ir/Cu system, but applies to a much wider class of systems, and holds also for defects in deeper layers. For the Ir/Cu-system we confirm by total energy calculations that the sub-surface position is energetically the most favorable one.

Acknowledgement includes: Program Training and Mobility of Researchers 'Interface Magnetism' (Contract: EMRX-CT96-0089) and 'Electronic Structure' (Contract: FMRX-CT98-0178) of the European Union.

(accepted in Phys. Rev. Lett.)
copy available from: s.bluegel@fz-juelich.de

First-principles theory of ultra-thin magnetic films

T. Asada†, G Bihlmayer, S Handschuh, S Heinze¶, Ph Kurz, and S Blügel
†*Faculty of Engineering, Shizuoka University,*
Hamamatsu 432-8002, Japan
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany
¶*Zentrum für Mikrostrukturforschung, Universität Hamburg,*
D–20355 Hamburg, Germany

Abstract

We report on a set of systematic first-principles electronic-structure investigations of the magnetic spin moments, the magnetic spin configurations, and the magnetic coupling of ultrathin magnetic films on (001) and (111) oriented noble-metal substrates and on the Fe(001) substrate. Magnetism is found for $3d$, $4d$, and $5d$ transition-metal monolayers on noble metal substrates. For V, Cr, and Mn on (001) substrates a c(2×2) antiferromagnetic superstructure has the lowest energy, and Fe, Co, Ni are ferromagnetic. On (111) substrates, for Cr the energy minimum is found for a 120° non-collinear magnetic configuration in a $(\sqrt{3}\times\sqrt{3})$R30° unit cell, and for Mn a row-wise antiferromagnetic structure is found. On Fe(001), V and Cr monolayers prefer the layered antiferromagnetic coupling, and Fe, Co, and Ni monolayers favor the ferromagnetic coupling to Fe(001). The magnetic structure of Mn on Fe(001) is a difficult case: at least two competing magnetic states are found within an energy of 7 meV. The Cr/Fe(001) system is discussed in more detail as the surface-alloy formation is investigated and this system is used as test case to compare theoretical and experimental scanning tunneling spectroscopy (STS) results. The possibility to resolve magnetic structures by STS is explored. The results are based on the local spin-density approximation and the generalized gradient approximation to the density functional theory. The calculations are carried out with the full-potential linearized augmented plane-wave method in film geometry.

Acknowledgement includes: Program Training and Mobility of Researchers 'Interface Magnetism' (Contract: EMRX-CT96-0089) and 'Electronic Structure' (Contract: FMRX-CT98-0178) of the European Union.

(submitted to J. Phys. Condensed Matter, contribution to a special issue on surface magnetism)
copy available from: s.bluegel@fz-juelich.de

Electronic and magnetic structure of thin Ni films on Co/Cu(001)

S. S. Dhesi, H. A. Dürr, G. van der Laan, E. Dudzik, and N. B. Brookes
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, U.K.

Abstract

The electronic and magnetic structure of ferromagnetic Ni films grown epitaxially on ultrathin films of Co has been studied by x-ray absorption spectroscopy (XAS) using circular polarization. The growth morphology of the films was verified using high-resolution low-energy electron diffraction (HRLEED) and indicated an incomplete layer-by-layer growth mode for the Co and Ni films deposited on Cu(001). We report the presence of additional peaks in the x-ray magnetic circular dichroism (XMCD) as predicted by the configuration interaction model. The ground state magnetic moments were obtained from the XMCD sum rules at the Ni $2p$ edge. For a film thickness below 2 ML the number of holes and the spin polarization (spin moment per hole) show a gradual decrease, while the orbital polarization (orbital moment per hole) and the spin-orbit interaction show a gradual increase in magnitude. The 6 eV satellite structure, which is present in the XAS and XMCD of bulk Ni, disappears for submonolayer coverages while the dichroism due to “diffuse magnetism” between the L_3 and L_2 edges is strongly enhanced. These observations are ascribed to changes in the hybridization (electronic mixing) as a function of film thickness, which influences the ground state d^8 weight and the s state spin polarization. The strongly increased orbital moment per spin provides a good measure for the degree of localization. It is shown that for Ni thin films a localization of the wavefunction does not lead to an enhancement in the total magnetic moment, but on the contrary its value is twice as small as the bulk value.

(Accepted for Phys. Rev. B)
Preprints available from: g.vanderlaan@dl.ac.uk
Manuscripts available from:

Influence of magnetism for the alloy formation of ultrathin films

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Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany
T. Asada
Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

Abstract

In this article we review the present understanding of the interrelation between the energetic stability of surface alloys and magnetism, magnetic ordering, the choice of substrate and surface orientation. We discuss trends for $3d$-alloys on a Cu(100) surface and specifically present *ab initio* results for the formation energy and the interdiffusion energy of Mn surface alloy films on the Cu(100), (110) and (111) surface and on the Ag(100) and Ni(100) surfaces. Results based on the density-functional theory elucidate the origin of the existence of thermodynamically stable surface alloys. Although in detail, the results depend on the selected substrate/alloy combinations, the trends presented here have a universal character. Recently, several of these surface alloys have been found experimentally. The large structural corrugation of the surface alloy atoms and their enhanced magnetic moment contribute to the stabilization of the alloys. This will be discussed as a result of a large magneto-volume effect. Total energy and force calculations are carried out using the full–potential linearized augmented plane–wave (FLAPW) method in film geometry.

Acknowledgement includes: Program Training and Mobility of Researchers 'Interface Magnetism' (Contract: EMRX-CT96-0089) and 'Electronic Structure' (Contract: FMRX-CT98-0178) of the European Union.

accepted by World Scientific (International Symposium on Structure and Dynamics of Heterogeneous Systems)

copy available from: s.bluegel@fz-juelich.de

Surface Diffusion and Models for the Kinetics of Epitaxial Growth

K. Schroeder, A. Antons, R. Berger, Wi. Kromen, and S. Blügel
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

Abstract

We shortly review the surface processes relevant in epitaxy and discuss the conditions for the realization of different growth modes. We discuss the stability of 3-dimensional and 2-dimensional islands in terms of macroscopic thermodynamics and derive the critical island size. We introduce the kinetic equations governing epitaxy in the limit when island nucleation is the growth determining mechanism and discuss the important parameters. Finally, we discuss the action of surfactants, specifically of As, for homo-epitaxy and Ge hetero-epitaxy on Si(111). We present results of *ab initio* calculations for the rates of diffusion and incorporation of single Si, Ge, and Sn ad-atoms on As-terminated Si(111) and discuss growth models for these group-IV elements on Si(111):As.

accepted by World Scientific (International Symposium on Structure and Dynamics of Heterogeneous Systems)

copy available from: s.bluegel@fz-juelich.de

Electron-positron correlations in silicon

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Polish Academy of Sciences, P.O.Box 937, 50-950 Wrocław 2, Poland
Z. Szotek and W.M. Temmerman
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U.K.

Abstract

A number of approaches to treat the electron-positron correlation effects is used to study the electron-positron momentum densities and positron annihilation rates in silicon. Also, the nonlocal effects are explicitly taken into account within the weighted density approximation (WDA), giving rise to the nonlocal state-selective electron-positron correlation functions. The WDA results for the electron-positron momentum densities and annihilation rates are compared to the experimental data and to the calculations performed within the independent particle model and local density approximation. Additionally, the generalized gradient approximation is used to calculate the nonlocal, but state-independent, quantities. The importance of nonlocality and state-dependence of the electron-positron correlation functions, and the role of the positron wavefunction, are discussed in detail.

(Submitted to Phys. Rev. B)
Manuscripts available from: ania@int.pan.wroc.pl

Systematics for Trivalent and Divalent Rare Earth Sulphides

W.M. Temmerman[1], A. Svane[2], P. Strange[3], Z. Szotek[1], and H. Winter[4]
[1] *Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U.K.*
[2] *Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*
[3] *Physics Department, Keele University, Keele, Staffordshire, ST5 5BG, U.K.*
[4] *INFP, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany*

Abstract

The electronic structures of the rare earth monosulphides are calculated with the self-interaction corrected local-spin density approximation. This scheme allows part of the rare earth $f-$shell to be localized. Both trivalent and divalent configurations of the rare earths are considered, and the systematics in lattice constants and electronic densities of states are investigated. The scheme is found accurate in describing the properties of these systems, and reveals that two kinds of $f-$electrons in fact are present in the rare earth monosulphides, namely both localized atomic-like $f-$electrons and itinerant band $f-$electrons, which hybridize with the normal conduction bands. The stability of the divalent configuration directly correlates with the number of band $f-$electrons.

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

Dynamics of hydrogen dissociation at the sulfur-covered Pd(100) surface

A. Groß
Physik-Department T30, Technische Universität München,
85747 Garching, Germany
M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany

Abstract

We report calculations of the dissociative adsorption and associative desorption of H_2 at Pd(100) covered with 1/4 monolayer of sulfur using quantum dynamics as well as molecular dynamics and taking all six degrees of freedom of the two H atoms fully into account. The potential energy surface (PES) has been derived from density-functional theory calculations. The absolute value of the calculated sticking coefficient turns out to be at variance with a molecular beam experiment. However, the relative change of the sticking coefficient as a function of the angle of incidence as well as the mean kinetic energy and the rotational alignment of desorbing hydrogen molecules agree quite well with the experiment. This indicates that the calculated PES reproduces the most favorable reaction path, but that in the experiment the sulfur adlayer was probably not very well-ordered.

(submitted to: Phys. Rev. B)
Contact person: Axel Groß (agross@physik.tu-muenchen.de)

Theory of surfaces and interfaces of group-III nitrides

J. Neugebauer, T. K. Zywietz, M. Scheffler
Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany
J. E. Northrup
Xerox Palo Alto Research Center, 3333 Coyote Hill Rd., Palo Alto, CA 94304

Abstract

Employing first principles total energy calculations we have studied the structure and energetics of surfaces and interfaces in group III-nitrides and their alloys. Consequences for the morphology and stability of epitaxial layers will be discussed.

(submitted to: Appl. Surf. Sci.)
Contact person: Jörg Neugebauer (neugebauer@fhi-berlin.mpg.de)

Soft x-ray magnetic scattering from striped magnetic domain structures

G. van der Laan, E. Dudzik, S.P. Collins, S.S. Dhesi, H.A. Dürr
Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK
M. Belakhovsky, K. Chesnel, A. Marty, Y. Samson, and B. Gilles
CEA/Grenoble, Service de Physique des Materiaux et Microstructures,
17 Rue des Martyrs, 38054 Grenoble, France

Abstract

We show that the magnetization profile of magnetic patterns in thin films can be obtained by using circular dichroism to recover the phase relation in x-ray resonant magnetic scattering. This is demonstrated for single-crystalline FePd layers with striped magnetic domain pattern where we obtain unambiguous evidence for the presence of magnetic flux closure domains.

(Submitted to Physica B)
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Surface energetics, pit formation, and chemical ordering in InGaN alloys

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Abstract

We present first-principles calculations of the structure and energetics of the GaN($10\bar{1}1$) surface, and present models for the reconstructions. A strong preference for In surface segregation and for occupation of specific surface sites is demonstrated. We argue that inverted pyramid defect formation is enhanced by segregation of In on ($10\bar{1}1$) facets. We propose that the chemical ordering recently observed in InGaN alloys is driven by the preference for In incorporation at the sites of reduced N coordination present at step edges during growth on the (0001) and ($000\bar{1}$) surfaces.

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Equilibrium shapes and energies of coherent strained InP islands

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Abstract

The equilibrium shapes and energies of coherent strained InP islands grown on GaP have been investigated with a hybrid approach that has been previously applied to InAs islands on GaAs. This combines calculations of the surface energies by density functional theory and the bulk deformation energies by continuum elasticity theory. The calculated equilibrium shapes for different chemical environments exhibit the {101}, {111}, $\{\bar{1}\bar{1}\bar{1}\}$ facets and a (001) top surface. They compare quite well with recent atomic-force microscopy data. Thus in the InP/GaInP-system a considerable equilibration of the individual islands with respect to their shapes can be achieved. We discuss the implications of our results for the Ostwald ripening of the coherent InP islands. In addition we compare strain fields in uncapped and capped islands.

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Magnetic circular X-ray dichroism in emission for disordered Co-Rh-based ternary alloys

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Abstract

Fully relativistic investigations on the magnetic circular dichroism in emission have been performed for Rh in the alloy systems $\mathrm{Co}_{0.75}\mathrm{Rh}_{0.25}$, $\mathrm{Co}_{0.75-x}\mathrm{Rh}_{0.25}\mathrm{Ni}_x$ and $\mathrm{Co}_{0.75}\mathrm{Rh}_{0.25-x}\mathrm{Pd}_x$. The results obtained using the spin-polarized relativistic Korringa-Kohn-Rostoker method of band structure calculation together with the Coherent-Potential-Approximation (SPR-KKR-CPA) allow one a detailed interpretation of corresponding experimental data. The changes for the magnetic moments of Co and Rh in the binary alloy $\mathrm{Co}_x\mathrm{Rh}_{1-x}$ caused by substitution of Rh by Pd and Co by Ni, respectively, are discussed in comparison with experimental data and a generalized Slater-Pauling curve.

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Manuscript available as ps-file on request from H. Ebert (he@gaia.cup.uni-muenchen.de)

A relativistic theory for the nuclear spin-lattice relaxation rate in ferromagnetic metals with application to 5d impurities in bcc-Fe

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Abstract

A relativistic theory for the nuclear spin-lattice relaxation rate $(TT_1)^{-1}$ in ferromagnetic metals is presented that includes in particular the electric quadrupolar and the core polarization contributions. Because it is formulated within the framework of the spin-polarized relativistic version of the Korringa-Kohn-Rostoker (SPR-KKR) method of band structure calculations it can be applied in principle to any kind of system. Here an application of the theory to 5d impurities (Lu - Hg) in ferromagnetic bcc-Fe is presented. While the core polarization contribution turned out to be negligible in all cases, the electric quadrupolar contribution was found to be in the same order of magnitude as the magnetic dipolar one in the case of Lu, Hf, Ir and Au.

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Theoretical study of the magnetic properties and x-ray magnetic circular dichroism of the ordered $Fe_{0.5}Pd_{0.5}$ alloy

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Abstract

A detailed theoretical study of magnetic and structural properties of $Fe_{0.5}Pd_{0.5}$ ordered face-centered tetragonal (fct) alloy, using both the local spin density approximation (LSDA) and the generalized gradient approximation (GGA), is presented. The total energy surface as a function of the lattice parameters a and c shows a long valley where stable structures may exist. Our calculation using the GGA predicts a magnetic phase transition from perpendicular to parallel magnetization as a function of the lattices parameters. Whereas LSDA favors always the [001] magnetization axis for all values of the lattice parameters. The spin and orbital magnetic moments and x-ray magnetic circular dichroism (XMCD) spectra are calculated for the easy [001] and the hard [100] magnetization axis and for three sets of experimental lattice parameters, and are compared to the available experimental results on these films. A supercell calculation for a 4 monolayer $Fe_{0.5}Pd_{0.5}$ thin film produced similar results. While the spin magnetic moments are in fair agreement with experiment, the orbital magnetic moments are considerably underestimated. To improve the agreement with experiment we included an atomic orbital polarization term, however the computed orbital moments scarcely changed.

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Ab-initio ground state and $L_{2,3}$ x-ray magnetic circular dichroism of Mn-based Heusler alloys

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Abstract

Relativistic full-potential calculations within the generalized gradient-approximation (GGA) for a series of Mn-based Heusler alloys are presented. Calculated equilibrium lattice parameters deviate less than 1.2% from the experimental values. The main features of a half-metallic system are present in the density of states for the PtMnSb and NiMnSb. We predict that PdMnSb shows half-metallic character under hydrostatic pressure. The substitution of Sb in PtMnSb by Sn or Te destroys the minority spin band gap. Spin and orbital magnetic moments for all the systems are in good agreement with previous calculations and experimental data. $L_{2,3}$ x-ray absorption and x-ray magnetic circular dichroism (XMCD) spectra are calculated for all the five compounds. Pt spectra present big deviations from system to system in the PtMnY(Y=Sn,Sb,Te) compounds while Mn spectra show only small deviations. For all these spectra GGA underestimates the L_3/L_2 integrated branching ratio and produces a much smaller L_2 peak intensity for the Ni site in NiMnSb. The XMCD sum rules are used to compute the spin and orbital magnetic moments and the results are compared to the direct calculations.

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First-principles theory of 250,000-atom coherent alloy microstructure

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Abstract

Microstructural issues in alloys such as precipitation have largely been outside the realm of first-principles electronic structure calculations due to the length scales involved in precipitation microstructure (typically nanometers to microns) and the inherent thermodynamic/statistical nature of the problem. Here, we show that modern, first-principles total energy calculations can be combined with a mixed-space cluster expansion approach (a generalized real/reciprocal space Ising model), and Monte Carlo simulations to yield a method capable of describing equilibrium coherent precipitate shapes in alloys with system sizes up to 250,000 atoms. Both the interfacial free energies and the coherency strain between precipitate and matrix are accounted for in this method as well as the short-range atomic-scale ordering of the solid solution. Illustrations of the technique are given for several famous examples of coherent precipitation in aluminum alloys: Al-Mg, Al-Cu, and Al-Ni.

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First-principles prediction of equilibrium precipitate shapes in Al-Cu alloys

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Abstract

A first-principles thermodynamic approach for studying coherent precipitation in size-mismatched alloys is presented and applied to the well-studied (but still controversial) problem of Guinier-Preston (GP) zone formation in Al-Cu alloys. The exceptionally soft anharmonic elastic response of Cu along {100} is crucial in determining the shape of clusters of Cu atoms embedded in the Al matrix which are plate-like {100} structures. First-principles calculations involving both strain and interfacial energies yield two types of disc-shaped precipitates, GP1 and GP2, which are, respectively, single Cu monolayers and two monolayers separated by three Al layers, in agreement with many (but not all) measurements. Competition between the thermodynamic driving force (favoring GP2) and interfacial energy around the perimeter of the zones (favoring GP1) leads to a size-dependent transition in the equilibrium precipitate shape from GP1 to GP2 at ∼150Å. This theoretical approach - generally applicable to metals, ceramics, and semiconductors - should aid in understanding the coherent precipitate shapes in a variety of alloy materials.

(Phil. Mag. Lett. **79**, 683 (1999))
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Preprints from Center for Atomic-scale Materials Physics (CAMP)

- P.A. Korzhavyi, I.A. Abrikosov, B. Johansson, A.V.Ruban, and H.L. Skriver:
  First-principles calculations of the vacancy formation energy in transition and noble metals
  ,
  Phys.Rev. accepted
- J.Schiøtz and E.A. Carlsson:
  The influence of surface stress on dislocation emission from sharp and blunt cracks i f.c.c. metals,
  Phil.Mag.A accepted
- T. Rasmussen, T. Vegge, T. Leffers, O.B. Pedersen, and K.W. Jacobsen:
  Simulation of structure and annihilation of screw dislocation dipoles,
  Phil.Mag.A accepted
- J. Schiøtz and T. Vegge:
  Computer simulations of the mechanical properties of metals,
  Science Progress accepted
- J.H. Larsen and I. Chorkendorff:
  From fundamental studies of reactivity on single crystals to the design of catalysts,
  Surf.Sci.Rep. accepted
- J. Nerlov, S. Sckerl, J. Wambach, and I. Chorkendorff:
  Methanol synthesis from CO_2, CO, an H_2 over Cu(100) and Cu(100) modified by Ni and Co,
  J.Appl.Cat.A accepted
- K. Morgenstern, E. Lægsgaard, I. Stensgaard, F. Besenbacher, M. Böhringer, R. Berndt, F. Mauri, A. de Vita, R. Car, and W.-D. Schneider:
  Stability of two-dimensional nanostructures,
  J.Appl.Phys. accepted
- J. Schiøtz:
  Computer simulations of nanocrystalline metals,
  submitted
- L. Vitos, H.L. Skriver, and J. Kollár:
  From ASA towards full potential,
  submitted
- M. Mavrikakis, P. Stoltze, and J.K. Nørskov:
  Making gold less noble,
  submitted

- R.M. Watwe, H.S. Bengaard, J.R. Rostrup-Nielsen, J.A. Dumesic, and J.K. Nørskov:
  Theoretical studies of stability and reactivity of CH_x *species on Ni(111)*,
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- C. Bendtsen, O.H. Nielsen, and L.B. Hansen:
  Solving large nonlinear generalized eigenvalue problems from Density Functional Theory calculations in parallel,
  submitted

- L.S. Byskov, J.K. Nørskov, B.S. Clausen, and H. Topsøe:
  H_2 *activation on a transition metal sulfide - The role of flexibility*,
  submitted

- S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgaard, J.K. Nørskov, B.S. Clausen, H. Topsøe, and F. Besenbacher:
  The atomic-scale structure of single-layer MoS_2 *nano-clusters*,
  submitted

- L. Österlund, M.Ø. Pedersen, I. Stensgaard, E. Lægsgaard, and F. Besenbacher:
  Quantitative determination of adsorbate-adsorbate interactions,
  submitted

- L. Petersen, L. Bürgi, H. Brune, F. Besenbacher, and K. Kern:
  Comment on "Observation of two-dinmensional Fermi contour of a reconstructed Au(111) surface using Fourier transform scanning tunneling microscopy" by D. Fujita, K. Amemiya, T. Yakabe, H. Nejoh, T. Sato, and M. Iwatsuki [Surf.Sci 423, 160 (1999)],
  submitted

- T.R. Linderoth, S. Horch, L. Petersen, S. Helveg, M. Schønning, E. Lægsgaard, I. Stensgaard, and F. Besenbacher:
  Energetics and dynamics of Pt dimers on Pt(110)-(1×2),
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  Palladium nano-crystals on Al_2O_3*: Structure and adhesion energy*,
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  Surface chemistry in three dimensions - CO dissociation between two surfaces,
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10 SCIENTIFIC HIGHLIGHT OF THE MONTH

Spin fluctuations in nearly magnetic metals from ab-initio dynamical spin susceptibility calculations

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There has been renewed interest in spin fluctuations in materials close to magnetic order recently. This is due in part to a realisation that nearly critical magnetic fluctuations may be important factors governing the non-conventional properties of a wide range of materials which include the high T_c superconducting cuprates and heavy fermion systems [1]. The strongly correlated electrons in many of these systems however have meant that most theoretical work has concentrated on parameterised models in which the electronic motion is treated rather simply. Another complementary approach however is to use an ab initio theory such as Time Dependent Density Functional Theory (TDDFT) [2] but apply it to materials where it can be expected to work i.e. where the effects of electron correlations are not so important, but which otherwise have important similarities to the systems in question. For example with its perovskite structure containing transition metal(TM)-oxygen planes, Sr_2RuO_4 has several aspects in common with the HTC materials. But the presence of the 4d TM Ru rather than the narrower band 3d TM Cu means that electron correlation effects are smaller and therefore DFT-based calculations can provide a valuable starting point. Moreover its p-wave superconductivity at low temperature seems likely to be affected by spin fluctuations [3, 4, 5]. Concerning another example, the transition temperature separating paramagnetic and magnetically ordered phases of the cubic transition metal compound $MnSi$, which has the B20 crystal structure, is driven down to zero temperature upon the application of pressure. In the vicinity of the critical pressure for this quantum phase transition the system exhibits non- or marginal Fermi liquid properties [6].

With the objective of investigating the spin-fluctuations in nearly magnetic materials such as these we have recently devised and proven a new scheme for calculating the wave-vector and frequency dependent dynamic spin susceptibility of metallic systems [7] which is based on the Time Dependent Density Functional Theory (TDDFT) of Gross et al. [2] and as such is an all electron theory. This enables the temperature dependent dynamic spin susceptibility of metals and compositionally disordered alloys to be calculated. In this article we outline the scheme and describe briefly some of our results for systems which although structurally and compositionally simpler than the two mentioned above, are also close to magnetic phase transitions.

Theoretical models in which an effective action for the slow spin fluctuations is written down have contributed greatly to our understanding of the properties of itinerant electron systems close to magnetic order [6]. Recent work which can incorporate results from DFT-based 'Fixed Spin Moment' (FSM) electronic structure calculations, treats these fluctuations classically [8]. A Landau-Ginzburg-like energy functional is written down, a free energy constructed which includes terms describing the interactions between the fluctuations (the mode-mode coupling) and properties such as the static susceptibility, specific heat and resistivity calculated. The FSM electronic structure calculations can be used to determine the coefficients in this functional [8]. Many informative studies have been carried out. For those calculations with such a DFT basis, these still remain qualitative investigations because of the lack of a prescription for the effective number of modes to include in the theory and its variation with temperature [6]. Stoner single particle excitation effects are also largely ignored. Both these issues can be addressed by the development and application of methods to calculate the temperature dependent dynamic paramagnetic spin susceptibility of nearly magnetic materials. The development of dynamic susceptibility calculations is particularly pertinent now that inelastic neutron scattering experiments, such as the time of flight measurements, have developed to the extent that spin fluctuations in nearly magnetic metals can be accurately measured [9].

Over the past few years great progress has been made in establishing TDDFT [2]. Analogs of the Hohenberg-Kohn [10] theorems of the static density functional (DFT) formalism have been proved and rigorous properties found. By considering a paramagnetic metal subjected to a small, time-dependent external magnetic field, $\mathbf{b}(\mathbf{r}, t)$ which induces a magnetisation $\mathbf{m}(\mathbf{r}, t)$ and using TDDFT in [7] an expression for the dynamic paramagnetic spin susceptibility $\chi(\mathbf{q}, w)$ via a variational linear response approach can be derived [11]. Accurate calculations of dynamic susceptibilities from this basis have been scarce (e.g. [12]) because they are difficult and computationally demanding. In ref.[7] we showed that these problems can be mitigated by accessing $\chi(\mathbf{q}, w)$ via the corresponding *temperature* susceptibility $\bar{\chi}(\mathbf{q}, w_n)$ where w_n denotes a bosonic Matsubara frequency [13].

The dynamical spin susceptibility $\chi(\mathbf{q}, w)$.

The equilibrium state of a paramagnetic metal, described by standard DFT, has density $\rho_0(\mathbf{r})$ and its magnetic response function

$$\chi(\mathbf{r}t;\mathbf{r}'t') = \frac{\delta m[b](\mathbf{r},t)}{\delta b(\mathbf{r}',t')}|_{b=0,\rho_0} \tag{1}$$

is given by the following Dyson-type equation.

$$\chi(\mathbf{r}t;\mathbf{r}'t') = \chi_s(\mathbf{r}t;\mathbf{r}'t') + \int d\mathbf{r}_1 \int dt_1 \int d\mathbf{r}_2 \int dt_2 \chi_s(\mathbf{r}t;\mathbf{r}_1t_1) K_{xc}(\mathbf{r}_1t_1;\mathbf{r}_2t_2)\chi(\mathbf{r}_2t_2,\mathbf{r}'t') \tag{2}$$

χ_s is the magnetic response function of the Kohn-Sham non-interacting system with the same unperturbed density ρ_0 as the full interacting electron system, and

$$K_{xc}(\mathbf{r}t;\mathbf{r}'t') = \frac{\delta b_{xc}(\mathbf{r},t)}{\delta m(\mathbf{r}',t')}|_{b=0,\rho_0} \tag{3}$$

is the functional derivative of the effective exchange-correlation magnetic field with respect to the induced magnetisation. As emphasised in ref.[2] eq.1 represents an exact representation of the linear magnetic response. The corresponding development for systems at finite temperature in thermal equilibrium has also been described [11]. In practice approximations to K_{xc} must be made and this work employs the adiabatic local approximation (ALDA) [2] so that

$$\begin{aligned} K_{xc}^{ALDA}(\mathbf{r}t;\mathbf{r}'t') &= \frac{db_{xc}^{LDA}(\rho(\mathbf{r},t),m(\mathbf{r},t))}{dm(\mathbf{r},t)}|_{\rho_0,m=0}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \\ &= I_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \end{aligned} \tag{4}$$

On taking the Fourier transform with respect to time we obtain the dynamic spin susceptibility $\chi(\mathbf{r},\mathbf{r}';w)$.

For computational expediency we consider the corresponding *temperature* susceptibility [13] $\bar{\chi}(\mathbf{r},\mathbf{r}';w_n)$ which occurs in the Fourier representation of the temperature function $\bar{\chi}(\mathbf{r}\tau;\mathbf{r}'\tau')$ that depends on imaginary time variables τ,τ' and w_n are the bosonic Matsubara frequencies $w_n = 2n\pi k_B T$. Now $\bar{\chi}(\mathbf{r},\mathbf{r}';w_n) \equiv \chi(\mathbf{r},\mathbf{r}';iw_n)$ and an analytical continuation to the upper side of the real w axis produces the dynamic susceptibility $\chi(\mathbf{r},\mathbf{r}';w)$.

We can define a general system as having a crystal structure with lattice vectors $\{\mathbf{R}_i\}$ and where there are N_s non-equivalent atoms per unit cell. On the l^{th} of the N_s sublattices there are N_l possible atomic species with concentrations c_{α_l} ($\alpha_l = 1,\cdots,N_l$). In each unit cell the N_s atoms are situated at locations $\mathbf{a}_l, l = 1,\cdots,N_s$. On carrying out a lattice Fourier transform over the lattice vectors $\{\mathbf{R}_i\}$ we obtain the following Dyson equation for the temperature susceptibility

$$\begin{aligned} \bar{\chi}^{\alpha_l}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) \quad &= \quad \sum_{\gamma_{l'}}^{N_{l'}} \bar{\chi}_s^{\alpha_l\gamma_{l'}}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) \\ +\sum_{l''}^{N_s} \quad \int d\mathbf{x}''_{l''} \quad &\sum_{\gamma_{l''}}^{N_{l''}} \bar{\chi}_s^{\alpha_l\gamma_{l''}}(\mathbf{x}_l,\mathbf{x}''_{l''},\mathbf{q},w_n) I_{xc}^{\gamma_{l''}}(\mathbf{x}''_{l''})\bar{\chi}^{\gamma_{l''}}(\mathbf{x}''_{l''},\mathbf{x}'_{l'},\mathbf{q},w_n) \end{aligned} \tag{5}$$

with $\mathbf{x}_l$,$\mathbf{x}'_{l'}$ and $\mathbf{x}''_{l''}$ measured relative to atomic cells centred on $\mathbf{a}_l$, $\mathbf{a}_{l'}$ and $\mathbf{a}_{l''}$ respectively.

In terms of the lattice Fourier transform of the DFT Kohn-Sham Green function of the static unperturbed system

$$\begin{aligned} &\bar{\chi}_s^{\alpha_l\gamma_{l'}}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) = \\ &-\frac{1}{\beta}\sum_m \int \frac{d\mathbf{k}}{v_{BZ}} \langle G(\mathbf{x}_l,\mathbf{x}'_{l'}, \quad \mathbf{k},\mu+i\nu_m)\rangle_{\alpha_l\gamma_{l'}} \quad \langle G(\mathbf{x}'_{l'},\mathbf{x}_l,\mathbf{k}+\mathbf{q},\mu+i(\nu_m+w_n))\rangle_{\gamma_{l'}\alpha_l} \end{aligned} \tag{6}$$

where the integral is over the Brillouin zone of the lattice and $\mathbf{k}$, $\mathbf{q}$ and $\mathbf{k}+\mathbf{q}$ are all wavevectors within this Brillouin zone which has volume v_{BZ}. μ is the chemical potential and ν_m is a fermionic Matsubara frequency $(2n+1)\pi k_B T$. $\langle\cdots\rangle_{\alpha_l\gamma_{l'}}$ denotes an average over all configurations which have one site on sublattice l occupied by an α_l type of atom and another on sublattice l' occupied by a $\gamma_{l'}$ atom.

The Green function can be obtained within the framework of multiple scattering (KKR) theory [14] and this makes this formalism applicable to disordered alloys as well as ordered compounds and elemental metals, the disorder being treated by the Coherent Potential Approximation (CPA) [15].

To solve equation (5), we use a direct method of matrix inversion in which, for example, $\bar{\chi}_s$ is cast into matrixform of order $(\sum_{l=1}^{N_s} S_l N_l) \times (\sum_{l=1}^{N_s} S_l N_l)$ where S_l is the number of spatial grid points associated with an atomic cell on the l^{th} sublattice. Local field effects are thus fully incorporated. The full Fourier transform can then be constructed.

The most computationally demanding parts of the calculation are the convolution integrals over the Brillouin Zone which result from the expression for $\bar{\chi}_s$, eq. (6). Since all electronic structure quantities are evaluated at complex energies z, these convolution integrals have no sharp structure and can be evaluated straightforwardly by an application of the adaptive grid method of E.Bruno and B.Ginatempo [16] which has been found to be very efficient and accurate. In this method one can preset the level of accuracy of the integration by supplying an error parameter ϵ.

Once the temperature susceptibility $\bar{\chi}(\mathbf{q}, \mathbf{q}; w_n)$ has been calculated the dynamic susceptibility can be found. As discussed in ref. [13], for example, we can define the retarded response function $\chi(\mathbf{q}, \mathbf{q}, z)$ of a complex variable z. Since it can be shown [13] formally that $\lim_{z\to\infty} \chi(z) \sim 1/z^2$ and we can obtain $\chi(iw_n)$ from the above analysis it is possible to continue analytically to values of z just above the real axis, i.e. $z = w + i\eta$. In order to achieve this we fit our data to a rational function

$$\bar{\chi}(\mathbf{q}, \mathbf{q}, w_n) = \chi(\mathbf{q}) \frac{(1 + \sum_{k=1}^{M-2} U_k(\mathbf{q}) w_n^k)}{(1 + \sum_{k=1}^{M} D_k(\mathbf{q}) w_n^k)} \tag{7}$$

in which M is an even integer. This form *ensures* that the sum rule involving the static susceptibility $\chi(\mathbf{q})$ is satisfied, i.e.

$$\chi(\mathbf{q}) = \frac{2}{\pi} \int_0^\infty dw \frac{Im\chi(\mathbf{q}, \mathbf{q}, w)}{w} \tag{8}$$

We find that very good fits are obtained with small M for a wide range of w_n's, $M = 4$ for Pd whereas for Cr and its dilute alloys $M = 2$ making the analogy with an overdamped harmonic oscillator model very close.

Antiferromagnetic paramagnons in Cr and its dilute alloys.

This new scheme has been demonstrated very recently by an investigation into the nature of the spin fluctuations in paramagnetic Cr and compositionally disordered $Cr_{95}V_5$ and $Cr_{95}Re_5$ alloys with good agreement with experimental data [7]. For example, recent inelastic neutron scattering experiments [17, 9] have measured incommensurate AF 'paramagnons', persisting up to high frequencies in $Cr_{95}V_5$ which were also shown in our calculations.

Chromium is the archetypal itinerant anti-ferromagnet (AF) whose famous incommensurate spin density wave (SDW) ground state is determined by the nesting wave-vectors $\mathbf{q}_{nest}$ identified in the Fermi surface [17]. Chromium alloys also have varied AF properties [17] and their paramagnetic states have recently attracted attention owing, in part, to analogies drawn with the high temperature superconducting cuprates especially $(La_cSr_{1-c})_2CuO_4$ [17]. For example,

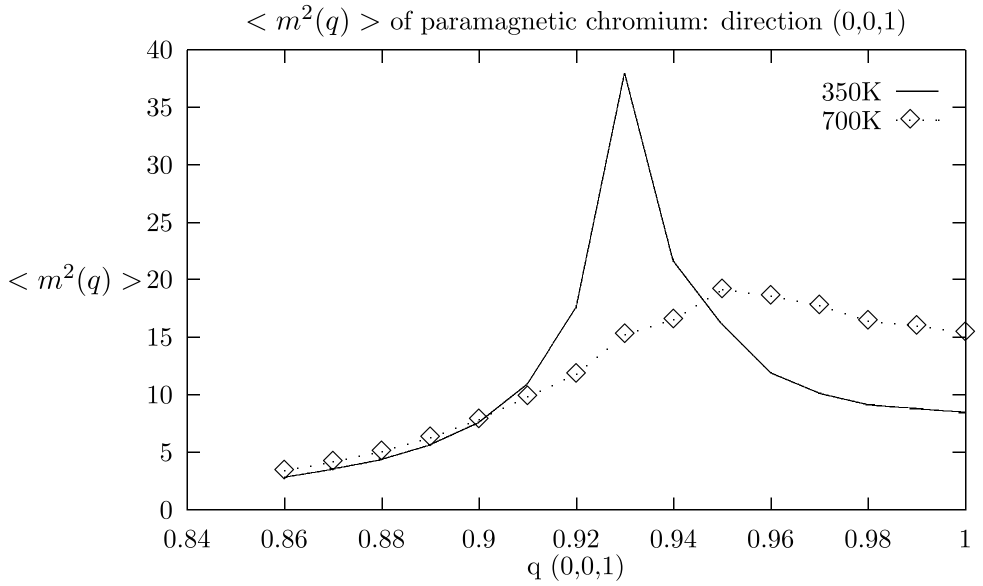

Figure 1: The variance of the spin fluctuations in paramagnetic Cr $< m^2(\mathbf{q}) >$ in μ_B^2 for wave-vectors $\mathbf{q}$ along the $\{0,0,1\}$ direction at 350K (full line) and 700K (dotted).

$Cr_{95}Mn_5$ or $Cr_{95}Re_5$ are simple commensurate AF materials which on lowering the electron concentration by suitable doping develop incommensurate spin fluctuations promoted by imperfectly nested Fermi surfaces. In [7] we explored the temperature dependence, variation with dopant concentration and the evolution of the spin fluctuations in these systems from incommensurability to commensurability with increasing frequency and provided the first ab-initio description of these effects [7]. Although there have been several simple parameterised models to describe the magnetic properties of Cr and its alloys [17], these have all concentrated on the approximately nested electron 'jack' and slightly larger octahedral hole pieces of the Fermi surface [17] and, at best, have only included the effects of all the remaining electrons via an electron reservoir. Whilst finding similarities between our results and results from such models we showed that a complete picture is obtained only when an electronic band-filling effect which favours a simple AF ordering at low temperature is also considered. We also found that the spin fluctuations are given an accurate description as overdamped diffusive simple harmonic oscillator modes which are at the heart of theories of the effects of spin fluctuations upon the properties of itinerant electron systems [6].

The nature of the spin fluctuations can be succinctly described via the variance $< m^2(\mathbf{q}) >$. From the fluctuation dissipation theorem, $< m^2(\mathbf{q}) >= (1/\pi) \int_{-\infty}^{\infty} dw(1-\exp(-\beta w))^{-1} Im\chi(\mathbf{q},\mathbf{q},w)$. Fig.1 shows $< m^2(\mathbf{q}) >$ at two temperatures for Cr where we have used a frequency cutoff of 500 meV and so have not included the faster of the quantum fluctuations. Near T_N the magnetic fluctuations have their greatest weight around the $\mathbf{q}_{nest}$. At higher T the peak diminishes and weight grows at $\mathbf{q}$'s nearer $\{0,0,1\}$ reflecting the shift in the peak in $Im\chi(\mathbf{q},\mathbf{q},w)$ from $\mathbf{q}_{nest}$ to commensurate $\mathbf{q}$'s with increase in frequency w.

The paramagnons of nearly ferromagnetic Pd.

We finish this article with a brief examination of the timescales associated with the spin fluctuations of Pd, a 4d transition metal so close to being a ferromagnet. Much has been written

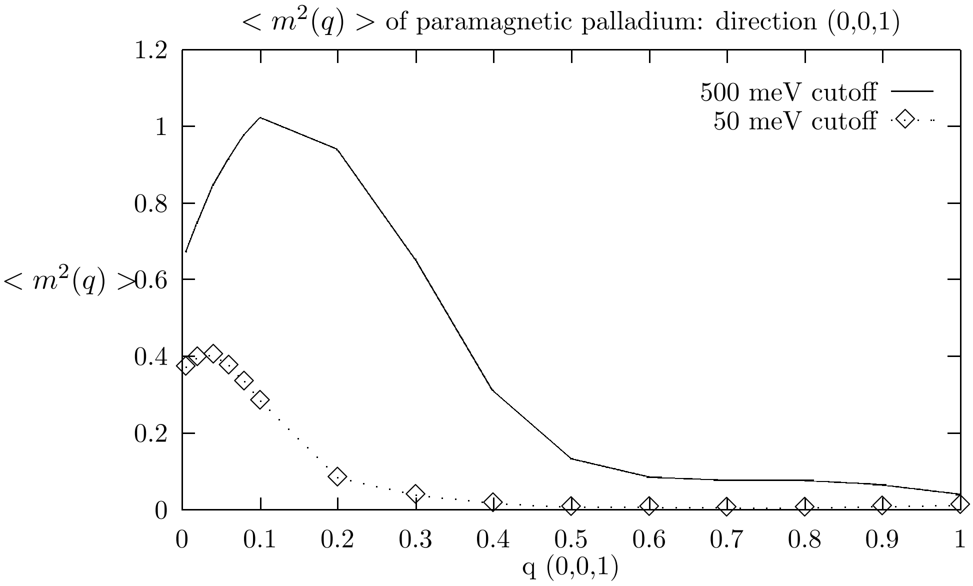

Figure 2: $< m^2(\mathbf{q}) >$ for wave-vectors $\mathbf{q}$ along $\{0, 0, 1\}$ in Pd at 100K with a frequency cutoff 500 meV (full line) and 50 meV (dotted).

about the low temperature spin fluctuations in this 4d transition metal especially those slow modes with long wavelength and in the context of possible p-wave superconductivity mediated by ferromagnetic paramagnons [18]. Fig.2 shows the magnetic correlations $< m^2(\mathbf{q}) >$ for Pd at 100K calculated using energy cutoffs of 500meV and 50meV. The paramagnons are clearly visible for a narrow region of small wave-vectors $\mathbf{q}$.

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