Ψ_k Newsletter

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

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Editor: Z. (Dzidka) Szotek
E-mail: psik-coord@dl.ac.uk

Contents

1 Editorial

We start this newsletter with some information on EC-funded Multi-disciplinary research opportunities under the heading 'HPC-Europa'. Following this we have some details on how to apply for the NSF funds to attend Psi-k2005 Conference in September 2005. In the section of the RTN2 network on "f-electrons" we have a mid-term review report of this network's activities over the past two years, including a few short scientific highlights. Reports on workshops, including abstracts of presented papers, can be found in the subsequent ESF section, where readers can also find an announcement of the XII INTERNATIONAL WORKSHOP ON COMPUTATIONAL PHYSICS AND MATERIALS SCIENCE: TOTAL ENERGY AND FORCE METHODS, to be held in Trieste. More workshop announcements can be found in the following section. Announcements of available positions and abstracts of newly submitted papers are in their usual sections. In the section one before last we have an announcement presenting a new initiative on "Bridging Time and Length Scales in Materials Science and Bio-Physics". The scientific highlight of this issue is on "Learn on the fly": a multiscale hybrid simulation method for material systems" by Gábor Csányi (Cambridge), T. Albaret (Villeurbanne), M. C. Payne (Cambridge), A. De Vita (London and Trieste). Please check the table of contents for further details.

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

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

The above contains information on the Psi-k 2004 workshops and hands-on courses. In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

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

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

2 General News

2.1 HPC-Europa: EC-funded Multi-disciplinary Research Opportunities

We would like to bring to your attention the existence of the HPC-Europa programme. This programme, fully funded by the European Commission, allows researchers from any scientific discipline to visit research groups located at any of our associated universities and research organisations for periods of two to 13 weeks. The emphasis of the programme is on High Performance Computing (HPC), a subject that naturally many of you will be involved in. The six participating sites are CEPBA (Barcelona), CINECA (Bologna), EPCC (Edinburgh), HLRS (Stuttgart), IDRIS (Paris), and SARA (Amsterdam).

The programme will cover the cost of accommodation, travel expenses, technical support by highly experienced staff, and access to some of the most powerful supercomputers in the world. Visiting researchers are hosted within the group with which they wish to collaborate for the duration of their visit.

The number of applications selected by our scientific committee currently stands at 60 %, so now is a good time to apply (next closing date: 15th November 2004 - and selections happen every 3 months). We expect competition for places to increase substantially once the programme becomes more well-known within the scientific community.

Further information, including eligibility criteria and guidelines for applications can be found at the HPC-Europa web site: www.hpc-europa.org.

Do not hesitate to contact us at access@hpc-europa.org should you require any further information. We hope that you and your colleagues will be interested by the opportunity offered by our programme.

Best wishes,
HPC-Europa team at EPCC

2.2 On how to apply for NSF funds to attend Psi-k2005 Conference

The US National Science Foundation has funded the Materials Computation Center at the University of Illinois to administer a program to support travel to European computational condensed matter workshops and schools, in particular PSIK and CECAM activities, for scientists from US Universities who could not otherwise attend. A particular focus is on junior scientists (i.e. students, post-docs and assistant professors) or scientists from under-represented groups and institutions.

Check http://www.mcc.uiuc.edu/travel/

for details and application procedures.

The MCC expects to support travel to the Psi-k2005 Conference (http://www.fyslab.hut.fi/psik2005) in Schwaebisch Gmuend, Germany to be held Sept. 17-21, 2005.

Applications will be due in early summer 2005.

3 News from the new RTN2 "f-electrons" Network "f-electrons"

3.1 Mid-term Review Report

RTN Network Title	:	Ab-initio Computation of Electronic Properties of f-electron Materials.
Network Short Title	:	Psi-k f-electron
Contract No.	:	HPRN-CT-2002-00295
Commencement date of contract	:	01-09-2002
Duration of Contract	:	48 months
Period covered by this report	:	26 months; 01-09-02 - 31-10-04

Name of co-ordinator	:	Associate Prof. Axel Svane
Organisation	:	University of Aarhus
Address	:	Department of Physics and Astronomy, Ny Munkegade, DK-8000 Aarhus C, Denmark
Telephone	:	+45 8942 3678
Telefax	:	+45 8612 0740
E-mail	:	svane@phys.au.dk

Network home page	:	http://www.phys.au.dk/˜svane/rtn.htm

Location of the mid-term review meeting : Institut Henri Poincare, Paris, France

Date and time of meeting : 10-12-04, at 09:30

PART A - RESEARCH RESULTS

A.1 Scientific Highlights

Methodological Developments

Several improvements of Dynamical Mean Field Theory (DMFT) methodology have been developed. Within the Exact Muffin Tin Orbital method a charge and self-energy self-consistent spin-polarized T-matrix plus FLEX (SPTF) scheme has been implemented [1], tested and first application to δ-Pu reported [2]. A continuous time, full-interaction vertex, multiorbital Quantum Monte Carlo (QMC) scheme for fermions has been developed and applied to the problem of the interplay of on-site Kondo effect and spin-dynamics (paper submitted). The QMC scheme has been generalized to allow for a non-diagonal and low-symmetry matrix form of the local temperature-dependent Green-function within the Nth order MTO method [3]. The extension of DMFT to clusters of correlated atoms has been implemented and applied to two widely different test systems [4,5]. The development of a systematic method for constructing effective models of correlated electron systems based on the GW method is on-going, first results being published [6] (Paris, Nijmegen, Rutgers and Uppsala teams).

A fully relativistic exact MTO (FREMTO) method has been developed including CPA to treat disorder, and a paper has just been submitted [7] (Nijmegen team).

A local version of the self-interaction corrected (L-SIC) local spin density approach has been developed. This is being tested for Ce and NiO. The L-SIC is implemented in the multiple scattering band theory and therefore the Green's function is easily evaluated. This allows to implement the CPA to treat not only substitutional disorder but also charge and spin disorder. While the full many-body interacting system with on-site Coulomb interactions can be described as a one-electron system in fluctuating charge and spin fields, we are presently engaged in developing the static approximation. Therefore, as a first approximation, the dynamics of the fluctuations are neglected, however still capturing an important part of the correlations which might be sufficient for many systems. A publication on application to the phase diagram of elemental Ce has been submitted [8]. Several applications to dilute Ce alloys and other alloy systems are in the pipeline (Daresbury and Aarhus teams).

A new LDA+U scheme for intermediate localization has been checked with the LDA+DMFT for the transition from magnetic to non-magnetic ground state for correlated metallic systems (Nijmegen team).

The full-potential local-orbital (FPLO) [50] method is being implemented for surfaces, the reduced symmetry aspect being already completed, yet awaiting the implementation of the appropriate multipole compensation method for the solution of the Poisson equation (Dresden team).

A new method to describe intermediate valence based on LDA calculations of the competing integral valencies has been developed and tested on the continuous pressure induced valence transition observed in Yb [9] (Uppsala and Nijmegen teams).

Pu and other actinides

The electronic structure of $PuO_{2\pm x}$ was studied using first-principles quantum mechanics, realized with the local spin density method, describing the energetics of f electron localization either with self-interaction corrections or empirical multiplet energies [10,11,51]. In the stoichiometric PuO_2 compound, Pu occurs in the Pu(IV) oxidation state, corresponding to a localized f^4 shell. If oxygen is introduced onto the octahedral interstitial site, the nearby Pu atoms turn into Pu(V) (f^3) by transferring electrons to the oxygen. Oxygen vacancies cause Pu(III) (f^5) to form by taking up electrons released by oxygen. At $T = 0$ the PuO_2 compound is stable with respect to free oxygen, but the delicate energy balance suggests the possible deterioration of the material during long-term storage (Aarhus, Daresbury and Uppsala teams). The crystal fields in PuO_2 have been calculated (Uppsala team).

The photoemission spectra of Pu and Pu compounds has been modelled by the LDA + Hubbard-I model, i.e. exact atomic self-energies including multiplet states are combined with accurate LDA band structure Hamiltonians. (Uppsala and Aarhus teams). The application to $PuCoGa_5$ [52] and PuSe shows that these systems are well described in terms of a mixed localized and delocalized f-manifold. The proposition of Wachter that the ground state of PuSe is similar to the high pressure phase of SmSe is confirmed. The method has also been applied to δ-Pu.

Other aspects of the relatively high-T_c superconductor, $PuCoGa_5$, most notably its Fermi surface properties have been investigated by conventional LSD calculations [12] (Dresden and Uppsala teams) as well as SIC-LSD (Aarhus team). The pairing of itinerant Pu $5f$ electrons has been identified as the cause of superconductivity. The calculated electron-phonon coupling strength does not appear significantly different from other Pu compunds, which are not superconductors, hinting at an unconventional origin of superconductivity in this compound.

The spectral function of δ-Pu at high temperature has been computed and compared with photoemission experiments (Nijmegen, Uppsala and Rutgers teams).

The trends in localization of the f shell in the series of actinide pnictides and chalcogenides [13] showed the relative destabilization of the f electrons in the earlier U and Np compounds towards primarily trivalent actinides in the Pu, Am and Cm compounds. At the same time the lighter ligands were found to destabilize the f electrons more than the heavier ones. The intricate U f electron manifold in UPd_2Al_2 has been investigated within the SIC-LSD approach [14], as has magnetism of UO_2 (Aarhus and Daresbury teams).

Rare Earth and Actinide Surfaces

The interpretation of scanning tunneling spectroscopy (STS) data taken on U/W(110) surfaces was facilitated by ab-initio calculation. It is demonstrated by fully relativistic total energy calculations including full optimization of all lattice parameters that the prepared structure can be a hexagonal Uranium phase, stabilized by the substrate, as seen in LEED and STM. Further, local densities of states are found to compare well with scanning tunneling spectra. This gives evidence for the possibility to observe f-states with STS [53] (Dresden team).

The lattice parameter and valence stability of the surface of Sm was calculated and good agreement with experimental photoemission work was demonstrated (Uppsala team).

Magnetism of Gd

The origin of the magneto crystalline anisotropy of hcp Gd has been subject to intense study. Several mechanism have been proposed, e.g. the mixing of higher multiplets into the otherwise spherically symmetric S-state, or the effect of relativity of the $5d$ valence band. The latter contribution has been shown to reproduce the experimental data with good accuracy. Based on Hartree-Fock theory the mixing in of high multiplet configurations to the $4f^7$ configuration is found to be very small [15] (Uppsala team).

The spontaneous anisotropic magnetostriction of hcp Gd has been investigated within the LSDA and the LSDA+U approximations. As a rough model for the paramagnetic state with persisting $4f$ moments several static antiferromagnetic arrangements were considered. The calculated values of the spontaneous volume magnetostriction are in reasonable agreement with the experiment, but the sign of the anisotropic magnetostriction is wrong in the LSDA+U approach [54] (Dresden team).

Rare Earth monopnictides and monochalcogenides

The electronic structure of Sm monopnictides and monochalcogenides has been investigated with the self-interaction corrected LSD method. The localized f^5 and f^6 shells of the ground-state of the pnictides and chalcogenides, respectively, are well described, as evidenced by the excellent quantitative agreement with the lattice constants and bulk modulii. The high pressure intermediate valence state of the chalcogenides is described by a mixture of f^5 localized shells and a partially occupied f-band [16]. The fundamental gap of the chalcogenides in their semiconducting phase is defined by excitations of a localized f electron into the conduction band. This we calculate by total energy differences. The absolute values of the gaps are only in fair agreement with experiment, while the pressure coefficient are excellent, i.e. similar trends to what is observed in conventional semiconductors [17] (Aarhus and Daresbury teams).

Eu chalcogenides, candidates for spin-filtering devices, as well as trends of magnetism through the series of rare earth nitrides have been studied with the same methodology [18,19].

Other rare earth systems

Full geometry optimization of both lattice parameters and the internal atom positions in the crystal unit cell has been completed for a series of cerium compounds including CeS, Ce_2S_3 and Ce_3S_4. Comparisons with available experimental structural data show a level of agreement which is typical for DFT-GGA calculations, i.e. deviations between computed and experimental structural parameters in the range of a few percent. Initial results for optical excitations has been obtained with the LDA+U method. As expected, the energy of the f-bands is very sensitive to the U parameter. Therefore, current research efforts are addressing the issue of a physically meaningful and consistent determination of U (LeMans team).

Metallic Magnetism in $LaCrSb_3$ has been investigated [55]. This system is a non-collinear ferromagnet with a spin reorientation at about 95 K. Coexistence of itinerant and localized spins at one and the same Cr site has been suggested to explain the experimental results. Strong arguments against this model have been presented on the basis of electronic structure calculations and re-evaluation of experimental information (Dresden team).

The electronic structure and magnetic properties of compounds formed between f electron materials and transition metals have revealed many intriguing properties, ranging from quenched orbital moments and electron states that are on the border between localized and delocalized. In addition these materials sometimes exhibit complex non-collinear magnetic interactions which have been studied theoretically for several of these systems. The agreement with experiment is good, and mechanisms that determine if a non-collinear or collinear magnetic coupling occurs have been identified [56] (Uppsala and Dresden teams).

The spin, charge and orbital order in $LaMnO_3$ and its relation to oxygen arrangements was studied by the Daresbury-Aarhus collaboration [20].

A.2 Joint Publications

Researchers in the network have published 35 joint research articles (network post-docs are underlined):

1. L. Chioncel, L. Vitos, I. A. Abrikosov, J. Kollar, M. I. Katsnelson, and A. I. Lichtenstein *Ab initio electronic structure calculations of correlated systems: An EMTO-DMFT approach,* Phys. Rev. B**67**, 235106 (2003) KUN and UU partners.

2. L. V. Pourovskii, M. I. Katsnelson, and A. I. Lichtenstein, *Local perturbative approach to electronic structure in correlated f-electron systems: applications to Pu*, Bull. Am. Phys. Soc.: http://www.aps.org/meet/MAR04/baps/abs/S4380010.html KUN and UU partners.

3. E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, O.K. Andersen, *Mott transition and suppression of orbital fluctuations in orthorhombic* $3d^1$ *perovskites*, Phys. Rev. Lett **92**, 176403 (2004) ENS-ULM and KUN partners.

4. A. I. Poteryaev, A. I. Lichtenstein, and G. Kotliar, *Non-local Coulomb Interactions and Metal-Insulator Transition in* Ti_2O_3*: A cluster LDA+DMFT approach*, Phys. Rev. Lett. **93**, 86401 (2004). KUN and RUTGERS partners.

5. T. Giamarchi, S. Biermann, A. Georges, and A. Lichtenstein, *Dimensional cross-over and deconfinement in Bechgaard salts*, J. Physique IV **114**, 23 (2004). ENS-ULM and KUN partners.

6. F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein, *Frequency-dependent local interactions and low-energy effective models from electronic structure calculations*, cond-mat 0401620 (2004). ENS-ULM, KUN and RUTGERS partners.

7. L. V. Pourovskii, A. V. Ruban, L. Vitos, H. Ebert, B. Johansson, and I. Abrikosov, *Fully relativistic spin-polarized exact muffin-tin-orbitals method*, submitted to Phys. Rev. B (2004). KUN and UU partners.

8. M. Lüders, A. Ernst, M. Däne, Z. Szotek, A. Svane, D. Ködderitzsch, W. Hergert, B. Györffy and W. M. Temmerman, *Self-interaction correction in multiple scattering theory*, cond-mat 0406515 (2004). UAA and CCLRC partners with external team member Bristol.

9. M. Colarieti-Tosti, M. I. Katsnelson, S. Simak, R. Ahuja, B. Johansson, and O. Eriksson, *First principles electronic structure calclations for intermediate valence systems*, Phys. Rev. Lett, **93**, 96403 (2004). UU with KUN and external team member ITU-Karlsruhe.

10. L. Petit, A. Svane, Z. Szotek, and W. M. Temmerman, *First Principles Calculations of* $PuO_{2\pm x}$, Science, **301**, 498 (2003). UAA and CCLRC partners.

11. L. Petit, A. Svane, Z. Szotek, and W.M. Temmerman, *SIC-LSD study of* δPu *and* $PuO_{2\pm x}$, Mat. Res. Soc. Symp. Proc. **802**, DD6.7.1, (2004). UAA and CCLRC partners.

12. I. Opahle, S. Elgazzar, K. Koepernik, and P. M. Oppeneer, *Electronic Structure of the Pu-based superconductor* $PuCoGa_5$ *and of related actinide-115 compounds*, Phys. Rev. B **70**, 104504 (2004). IFW-DRESDEN and UU partners.

13. L. Petit, A. Svane, Z. Szotek, and W.M. Temmerman, *Self-interaction Corrected Calculations of Correlated* f*-electron Systems* Mol. Phys. Rep. **38**, 20 (2003). UAA and CCLRC partners.

14. L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, *Ab-initio study of the localized/delocalized* f*-manifold in* UPd_2Al_3, Europhys. Lett. **62**, 391 (2003). UAA and CCLRC partners.

15. M. Colarieti-Tosti, S. Simak, R. Ahuja, O. Eriksson, L. Nordström and M. S. S. Brooks, *On the magnetic anisotropy of Gd metal* Phys. Rev. Lett. **91** 157201 (2003). UU with external team member ITU-Karlsruhe.

16. A. Svane, V. Kanchana, G. Vaitheeswaran, W.M. Temmerman, Z. Szotek, P. Strange, L. Petit, and G. Santi, *Electronic Structure of Samarium Monopnictides and Monochalcogenides*, (Phys. Rev B. accepted, 2004). UAA and CCLRC partners with external team member Keele.

17. A. Svane, G. Santi, Z. Szotek, W. M. Temmerman, P. Strange, M. Horne, G. Vaitheeswaran, V. Kanchana, and L. Petit, *Electronic Structure of Sm and Eu Chalcogenides*, Phys. Stat. Sol. (b) **241**, 3185 (2004). UAA and CCLRC partners with external team member Keele.

18. M. Horne, P. Strange, W. M. Temmerman, Z. Szotek, A. Svane and H. Winter, *The electronic structure of Europium Chalcogenides and Pnictides*, J. Phys. Condens. Matter **16**, 5061 (2004). UAA and CCLRC partners with external team member Keele.

19. M. Aerts, P. Strange, M. Horne, W. M. Temmerman, Z. Szotek, and A. Svane, *Half-Metallic to Insulating Behaviour of Rare Earth Nitrides*, Phys. Rev. B **69**, 045115 (2004). UAA and CCLRC partners with external team member Keele.

20. R. Tyer, W. M. Temmerman, Z. Szotek, A. Svane, L. Petit, and G.A. Gehring, Ab initio *charge, spin and orbital energy scales in manganites*, Europhys. Lett. **65**, 519 (2004). UAA and CCLRC partners.

21. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *Half-metallic transition metal oxides*, J. Magn. Magn. Mater. **272-276**, 1816 (2004) UAA and CCLRC partners.

22. G. M. Stocks, W. M. Temmerman, Z. Szotek, A. Svane, D. Ködderitzsch, and H. Winter, *LSD-SIC studies of localization in the 4d-transition metal oxides* $SrRu_2O_4$ *and* $CaRu_2O_4$. J. Magn. Magn. Mater. **272-276**, 122 (2004) UAA and CCLRC partners.

23. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *Ab initio Study of Charge Order in* Fe_3O_4, Phys. Rev. B. **68**, 054415 (2003). UAA and CCLRC partners.

24. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, and H. Winter, *Electronic Structure of half-metallic double perovskites*, Phys. Rev. B. **68**, 104411 (2003). UAA and CCLRC partners.

25. Z. Szotek, W. M. Temmerman, D. Ködderitzsch, W. Hergert, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *SIC-LSD Description of Half-metallic transition metal oxides*, Mol. Phys. Rep. **38**, 11 (2003) UAA and CCLRC partners.

26. S. Pankov, S. Florens, A. Georges, G. Kotliar, S. Sachdev, *Non-Fermi liquid behavior from two-dimensional antiferromagnetic fluctuations: a renormalization-group and large-N analysis*, Phys. Rev. B. **69** , 054426 (2004) ENS-ULM and RUTGERS partners.

27. D. W. Boukhvalov, E. Z. Kurmaev, A. Moewes, D. A. Zatsepin, V. M. Cherkashenko, S. N. Nemnonov, L. D. Finkelstein, Yu. M. Yarmoshenko, M. Neumann, V. V. Dobrovitski, M. I. Katsnelson, A. Lichtenstein, B. N. Harmon and P. Kögerler, *Electronic Structure*

of magnetic molecules V_{15}*: LSDA+U calculations, x-ray emissions, and photoelectron spectra*, Phys. Rev. B **67**, 134408 (2003) KUN and UU partners.

28. A. Perlov, S. Chadov, H. Ebert, L. Chioncel, A. I. Lichtenstein and M. I. Katsnelson, *Ab-initio calculations of the optical and magneto-optical properties of moderately correlated systems: accounting for correlation effects*, Proceedings of the Conference: 'Physics of Spin in Solids: Materials, Methods & Applications', ed. S. Halilov, p. 161 (Kluwer Academic Publishers, Dordrecht, 2004). KUN and UU partners.

29. M. I. Katsnelson and A. I. Lichtenstein, *Magnetic susceptibility, exchange interactions and spin-wave spectra in the local spin density approximation*, J. Phys. Condens. Mat. **16**, 7439 (2004). KUN and UU partners.

30. L. Chioncel, M. I. Katsnelson, R. A. de Groot, and A. I. Lichtenstein, *Nonquasiparticle states in the half-metallic ferromagnet NiMnSb*, Phys. Rev. B **68**, 144425 (2003). KUN and UU partners.

31. L. Petit, T. C. Schulthess, A. Svane, W.M. Temmerman and Z. Szotek, *Valencies of Mn impurities in ZnO*, Mat. Res. Soc. Symp. Proc. **825E**, G2.9.1, (2004). UAA and CCLRC partners.

32. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, P. Strange, G. M. Stocks, D. Ködderitzsch, W. Hergert, and H. Winter, *Electronic Structure of Half-Metallic Ferromagnets and Spinel Ferromagnetic Insulators*, J. Phys. Condens. Matter (accepted 2004). UAA and CCLRC partners with external team member Keele.

33. A. V. Ponomareva, E. I. Isaev, L. V. Pourovskii, Yu. Kh. Vekilov, B. Johansson, and I. A. Abrikosov, *Ab-initio investigations of surface magnetism in V-Mo*, J. Magn. Magn. Mater, **272-276**, 1198 (2004). UU and KUN partners.

34. E. Holmström, A. Bergman, L. Nordström, I. Abrikosov, S. B. Dugdale, and B. L. Györffy, *The Fermi surface effect om Magnetic Interlayer Coupling*, cond-mat/0402093. UU with CCLRC external team member Bristol.

35. Zs. Major, S. B. Dugdale, R. J. Watts, G. Santi, M. A. Alam, S. M. Hayden, J. A. Duffy, J. W. Taylor, T. Jarlborg, E. Bruno, D. Benea, and H. Ebert, *Direct observation of the multi-sheet fermi surface in the strongly correlated transition metal compound* $ZrZn_2$, Phys. Rev. Lett. **92**, 107003 (2004). UAA with CCLRC external team member Bristol.

Single-institution post-doc Publications

36. F. Lecherman, S. Biermann, and A. Georges, *Importance of inter-orbital charge transfers for the metal-to-insulator transition of* $BaVS_3$, cond-mat/0409463 (2004).

37. A. Floris, G. Profeta, N. N. Lathiotakis, M. Lüders, M. A. L. Marques, C. Francini, E. K. U. Gross, A. Continenza, and S. Massidda, *Superconducting properties of* MgB_2 *from first principles*, cond-mat/0408688 (2004).

38. M. Lüders, M. A. L. Marques, N. N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda, and E. K. U. Gross, *Ab-initio theory of superconductivity-I: density functional formalism and approximate functionals*, cond-mat/0408685 (2004).

39. M. A. L. Marques, M. Lüders, N. N. Lathiotakis, G. Profeta, A. Floris, L. Fast, A. Continenza, E. K. U. Gross, and S. Massidda, *Ab-initio theory of superconductivity-II: application to elemental metals* cond-mat/0408686 (2004).

40. M. Wierzbowska, M. Lüders, and E. Tossatti, *Multiplet structures of charged fullerenes*, J. Phys. B: At. Mol. Opt. Phys. **37**, 2685 (2004).

41. A. Ernst and M. Lüders, *Methods for band structure calculations in solids*, in 'Computational Material Science - From basic principles to material properties', eds. A. Ernst, M. Däne, and W. Hergert, Lecture Notes in Physics, Vol. 642 (2004).

42. N. N. Lathiotakis, M. A. L. Marques, M. Lüders, L. Fast, and E. K. U. Gross, *Density functional theory for superconductors*, Int. J. Quant. Chem. **99**, 790 (2004).

43. M. Lüders, N. Manini, P. Gattari, and E. Tossatti, *Hund's rule magnetism in* C_{60} *ions?*, Eur. Phys. J. **B35**, 57 (2003).

44. M. Lüders and N. Manini, *Jahn-Teller distortions and excitation energies in* C_{60}^{n+} , Adv. Quantum Chem. **44**, 289 (2003).

45. F. Lecherman, M. Fäehnle, and J. M. Sanchez, *First-principles investigation of the Ni-Fe-Al system*, cond-mat/0410285 (2004).

46. F. Lecherman, M. Fäehnle, B. Meyer, and C. Elsässer, *Electronic correlations, magnetism, and structure of Fe-Al subsystems: An LDA+U study*, Phys. Rev. B **69** 165116 (2004).

47. R. Laskowski and G. Santi, *The role of inter-atomic non-collinear magnetization density in weak ferromagnetism*, cond-mat/0408200.

48. P. Ziesche and F. Tasnadi, *Reduced density matrices, their spectral resolutions, and the Kimball-Overhauser approach*, Ann. d. Phys. **13**, 232 (2004).

49. P. Ziesche and F. Tasnadi, *The 2-matrix of the spin-polarized electron gas: contraction sum rules and spectral resolutions*, Ann. d. Phys. **13**, 124 (2004).

Significant single-institution publications

50. H. Eschrig, M. Richter, and I. Opahle, *Relativistic Solid State Calculations*, in: 'Relativistic Electronic Structure Theory - Part II: Applications', ed. by P. Schwerdtfeger, (Elsevier, Amsterdam 2004), p. 723.

51. P. A. Korzhavyi, L. Vitos, D. A. Andersson, and B. Johansson, *Oxidation of plutonium dioxide*, Nature Materials **3**, 225 (2004).

52. J. J. Joyce, J. M. Wills, T. Durakiewicz, M. T. Butterfield, E. Guziewicz, J. L. Sarrao, L. A. Morales, A. J. Arko, and O. Eriksson, *Photoemission and the electronic structure of* $PuCoGa_5$, Phys. Rev. Lett. **91**, 176401 (2003).

53. L. Berbil-Bautista, T. Hänke, M. Getzlaff, R. Wiesendanger, I. Opahle, K. Koepernik, and Manuel Richter, *Observation of 5f-states on U/W(110) films by means of Scanning Tunneling Spectroscopy*, Phys. Rev. B **70**, 113401 (2004).

54. U. Nitzsche, M. Richter, I. Chaplygin, K. Koepernik, I. Opahle, and H. Eschrig, *Electronic Structure and Magnetostriction in Bulk Gadolinium*, J. Magn. Magn. Mat. **272–276**, E249-E250 (2004).

55. M. Richter, J. Rusz, H. Rosner, K. Koepernik, I. Opahle, U. Nitzsche, and H. Eschrig, *Unconventional Metallic Magnetism in* $LaCrSb_3$, J. Magn. Magn. Mat. **272–276**, E251-E252 (2004)

56. M.D. Kuz'min, Y. Skourski, D. Eckert, M. Richter, K.-H. Müller, K.P. Skokov, I.S. Tereshina, *Spin reorientation in high magnetic field and the Co-Gd exchange field in* $GdCo_5$, Phys. Rev. B, in press.

The complete list of Network publications can be viewed on the Network homepage.

PART B - COMPARISON WITH THE JOINT PROGRAMME OF WORK

B.1.: Research Objectives

The research objectives of the Network are theoretical investigations of the physical properties of materials containing atoms with incompletely filled f-shells. These objectives remain unchanged with respect to the work programme of the contract, being still relevant and achievable. The research of the Network project has two threads: **a)** the application of existing methodology to specific scientific problems of high current priority, and **b)** the development of new methodology for a more accurate description of f-electron systems.

B.2.: Research Method

The research methodology of the Network is *ab-initio* quantum mechanics based upon Density Functional Theory and enhanced with the Dynamical Mean Field Theory capability. This is unchanged with respect to the work programme of the contract.

B.3.: Workplan

The Network Workplan is largely unchanged with respect to the contract. The major breakdown in 6 tasks is still valid.

- **Schedule and Milestones**

The Work Program comprises the following sub-projects: Milestones for first results of each of the subtasks are given in bold.

1. **Dynamical Mean Field Theory in the Linear Muffin-Tin-Orbital method** (Task leader: ENS-ULM, collaborating with UAA, CCLRC, RUTGERS, KUN and UU)

   1.1 Impurity solvers.

      1.1.A IPT (**12 months**) Implementation of self-consistent (in charge density and local self-energy (DMFT)) spin-polarized T-matrix plus FLEX (SPTF) scheme has been completed within the Exact MTO-method and paper published.

      1.1.B Extended NCA and other new impurity solvers. (**24 months**) Extended NCA is likely to be abandoned at the expense of better tools. Solution of impurity cluster problem is implemented. Exact diagonalization of relativistic atom interacting with dispersionless bath.

      1.1.C QMC (**18 months**) Continuous time, full-interaction vertex, multiorbital QMC scheme for fermions has been developed. First applications (5-orbital model) done. This QMC-scheme will be used for calculation of Ce on Ag(111) surface (task 3.3). QMC with NMTO implementation of Hamiltonian has been tested (generalized QMC scheme for non-diagonal, low-symmetry matrix form of the local temperature-dependent Green-function within NMTO-TB) This scheme will be useful for complex d- and f-compounds. First application for transition-metal perovskite published.

1.2 Green's Functions.

  1.2.A $T = 0$, full self-energy (**24 months**) A significant development of the DMFT methodology is towards the integration with the GW-approximation, which combines the DMFT treatment of strongly correlated degrees of freedom with approximate (random-phase-approximation) treatment of screening of the nearly-free electron degrees of freedom. This rather ambitious development most likely will outdate the IPT and extended NCA impurity solvers in terms of accuracy. On the other hand the technical problems in connection with generating a full GW-DMFT self-energy are large, and a realistic milestone is more likely 36 months. First papers on formalism published.

  A second new development is that of Cluster-DMFT. Within this scheme non-local spin and orbital fluctuations can be investigated. Several applications in joint publications.

  1.2.B Finite T (**36 months**) Awaits the completion of 1.2.A. The optical conductivity of Ce at high temperature has been calculated.

1.3 Combine 1.1 with 1.2 (**24 months**) In progress.

1.4 Include phonons in 1.3. (**48 months**) First effects of phonons included in discussion of δ-Pu.

2. **Actinides:** (Task leader: UU, collaborating with UAA, CCLRC, RUTGERS, IFW-DRESDEN, KUN, and ENS-ULM)

   2.1 **Phase Diagram of Pu** (sub-task leader: RUTGERS)

      2.1.A δ-phase ($T = 0$: **18 months**, finite T: **48 months**) Several attacks on the Pu δ-phase have been made by network partners ($T = 0$). Spectral functions for high-temperature have been compared with photoemission experiments. Start of calculations of δ-Pu with QMC in LDA+DMFT scheme.

      2.1.B ϵ-phase ($T = 0$: **18 months**, finite T: **48 months**) Has been initiated.

      2.1.C α-phase (**36 months**) Has not yet been initiated.

      2.1.D Pu compounds (**36 months**) The superconducting $PuCoGa_5$ compound has attracted quite extensive interest, and several Network contributions have been published in the past year. Also, the Pu valency and crystal field splitting in the PuO_2 compound has been investigated, and several joint publications published.

   2.2 Am and compounds. (**24 months**, finite T: **48 months**) Disordered local moments theory of actinide metals has been investigated and a paper completed. The trends of f-electron localization through the actinide chalcogenides and pnictides has been studied...

   2.3 Np (**24 months**) and compounds. ..including NpPn and NpCh...

   2.4 U (**24 months**) and compounds. ...as well as UPn and UCh! The U valency in UX_3 compounds has been investigated, revealing a shift towards greater localization through the series X=Rh, Pd, Pt, Au. Non-collinear magnetism of UO_2 has been studied and paper published. U adlayers on W surfaces have been studied (also part of task 4) and paper published.

3. **Rare-earth systems:** (Task leader: KUN, collaborating with UAA, CCLRC, RUTGERS, IFW-DRESDEN, ENS-ULM, UU and MD)

   3.1 Ce (**24 months**, finite T: **48 months**) Improved and simplified SIC methodology has been developed and tested on the $\alpha \rightarrow \gamma$ phase transition of Ce, including finite T. The high temperature optical conductivity of Ce in both the α and the γ phase has been calculated within DMFT.

   3.2 Optical properties of pigments such as Ce_2S_3 (**36 months**) (sub-task leader: MD) Geometry optimizations for CeS, Ce_2S_3 and Ce_3S_4 compounds have been completed. Initial results for optical excitations have been obtained with the LDA+U method.

   3.3 Ce on Ag(111) (**24 months**) DMFT methodology development completed. No results to report. Ce impurities in bulk metals have been calculated by the L-SIC method, and work on surfaces is in progress.

   3.4 SmS and TmSe (**36 months**) (sub-task leader: UAA) SmX compounds and their isostructural high pressure phase transitions have been studied and two joint papers published. TmSe work is in progress.

3.5 rare-earths in high-T_c superconductors (**18 months**) (sub-task leader: CCLRC) Several RE-$Ba_2Cu_3O_{6+x}$ compounds have been studied, with rather inconclusive results so far due to high sensitivity to structural details.

3.6 luminescence (**48 months**) Nothing has been initiated.

3.7 magneto-caloric materials (**36 months**) (sub-task leader: UU) Nothing has been initiated.

4. **Surface magnetism:** (Task leader: IFW-DRESDEN, collaborating with CCLRC, UU and MD)

4.1 Gd(0001) and related systems (**18 months**) In a study of the Sm(0001) surface the Sm atoms have been shown to exhibit divalency, as opposed to the trivalency of bulk Sm. Magnetic anisotropy has been investigated by LSD and LDA+U methods in bulk (hcp) Gd.

4.2 non-collinear moments (**30 months**) Non-collinear moments of (bulk) $LaCrSb_3$ and UO_2 were studied.

5. **Workshops:** (Task leaders: UAA and CCLRC, involves all partners)

5.1 5 Annual progress workshop (**0-1, 12, 24, 36 and 48 months**) A Euresco conference was organized by CCLRC and ENS-ULM partners cosponsored by the network in August 2003. The first annual meeting was organised in November 2003 in Aarhus with 35 attendees. Second annual meeting and midterm review is scheduled for december 2004 in Paris. A winterschool on the physics of the lighter actinides was organised in Riksgränsen, Sweden in May (37 attendees).

5.2 DFT and DMFT tutorial workshop (**18 months**) DMFT tutorial workshop was organized in Daresbury in June 2003.

5.3 Industry workshop (**36 months**) (sub-task leader: MD) Scheduled for 2006.

5.4 Hands-on course (**48 months**) FPLO hands-on-courses were organized in Dresden in March 2003 and in UC Davis, USA in June 2004 (latter not network financed). KKR as well as FPLO hands-on-courses are scheduled for spring 2005. A hands-on-DMFT course will take place in 2005.

6. **Newsletter and Home page:** (Task leader: CCLRC, involves all partners) Newsletters have been published every second month. The maintenance of the network homepage has been outsourced to partner UU.

- **Research Efforts of the Participants**

The research efforts of the Participants are summarized as follows:

Involvement								
task	UAA	CCLRC	RUTGERS	DRESDEN	KUN	ENS-ULM	UU	MD
1.1.A			x			**X**	x	
1.1.B	x		x		x	**X**		
1.1.C			x		x	**X**	x	
1.2.A	x	**X**	x		x	**X**	x	
1.2.B	x	**X**	x		x	**X**	x	
1.3	x	**X**	x		x	**X**		
1.4			**X**		x	x		
2.1.A	x	x	**X**		x		**X**	
2.1.B	x	x	x				**X**	
2.1.C			x				**X**	
2.1.D	x	x			x		**X**	
2.2	x	x	x	x	x	x	**X**	
2.3	x	x	x	x			**X**	
2.4	x	x	x	x	x		**X**	
3.1	x	x	x	x	**X**	x	x	
3.2	x						x	**X**
3.3					**X**			
3.4	**X**	x		x	x		x	
3.5	x	**X**						
3.6					**X**		x	
3.7							**X**	
4.1		x		**X**			x	x
4.2				**X**	x		x	x
5.1-4	**X**	**X**	x	x	x	x	x	x
6.1	x	**X**	x	x	x	x	x	x

Table 1: Involvement of the individual Research Teams. Task leaders are given in bold.

B.4.: Organisation and Management

B.4.1. Management.

The Network's scientific programme is broken down into sub-tasks each of which is managed by a board of two or more node leaders, coordinated through the Network Coordinator and the Network Secretary. The major part of network management happens through frequent email contact. Whenever appropriate, short-term secondments and mini-meetings between two or more network partners, including post-docs, are used to plan the near future scientific research programme of the sub-tasks. Major organisatorial planning is usually done in connection with Network meetings.

Network announcements, including abstracts of submitted papers, vacant positions, and network meetings, are announced in the bimonthly Psi-k newsletter, which currently is distributed to more than 1300 email addresses worldwide. The dissemination of scientific results is taking place through publication in research journals as well as presentations at conferences. Newsletters are available at:

http://psi-k.dl.ac.uk/index.html?newsletters

The Network home page is:

http://phys.au.dk/˜svane/rtn.htm

There has been a change of scientist-in-charge at partner KUN, as prof. A. I. Lichtenstein has accepted a chair at Hamburg University. Prof. M. I. Katsnelson, former employed at UU, has become new professor at KUN and has taken over the responsibility of scientist-in-charge. Since he has been part of the network since inauguration the change has been smooth. The collaboration with Prof. Lichtenstein continues.

B.4.2. Main network meetings.

- *FPLO hands-on-course*, Dresden March 28-April 1, 2003. 38 attendees.
- *DMFT tutorial session*, Daresbury June 5-6, 2003. 24 attendees. A. Georges and S. Biermann from partner ENS-ULM gave a series of tutorials on the basics of DMFT for newcomers in the field.
- *Ab initio Many-Body Theory for Correlated Electron Systems*, Trieste 25-29 August, 2003. This Euresco conference was organized by the CCLRC and ENS-ULM partners and cosponsored by the Network. 117 attendees.
- A bilateral mini-meeting between the ENS-ULM and KUN partners in Paris included

an External Expert, E. Pavarini, Pavia, Italy, who presented her implementation and investigations with the DMFT method in a seminar.

- The Karlsruhe external team member of the UU partner arranged a Actinide Users Meeting, where a substantial number of Network people attended.
- Network Board Meeting, Karlsruhe, Germany, March, 31 2003. 4 attendees.
- The autumn 2002 research workshop at Santa Barbara, US, *Realistic Theories of Correlated Electron Materials* was organised by the RUTGERS, KUN and ENS-ULM nodes, but did not involve Network finance.
- *The Physics of f-electron solids*, 1st annual Workshop, Århus, Denmark, Nov. 6-7, 2003. 35 attendees.
- Network Board Meeting, Århus, Denmark, Nov. 7, 2003. 7 attendees.
- Research Minimeeting, Århus, Denmark, Nov. 8-10, 2003. 6 attendees.
- Bilateral Research Meeting, Uppsala, Sweden, Nov. 19-21, 2003. 20 attendees.
- *Winter workshop on the electronic structure of the Light Actinides*, Riksgränsen, Sweden, May 11-16, 2004. 37 attendees.
- Network Board Meeting, Riksgränsen, Sweden, May 11, 2004. 7 attendees, including EU representative Jean-Paul Berhault.

B.4.3. Networking.

from to	UAA	CCLRC	RUTGERS	IFW	KUN	ENS	UU	MD
UAA		15,16a		16b	16c	16d	16e	16f
CCLRC	1,22	14,19				4	11	
RUTGS						23		
IFW	2						12	
KUN							13	
ENS			8		3			
UU	6,17a	7,17b,18	5	17c	17d,20,21		9, 17e	
MD								10

Table 2: Secondments and visits. Numbers refer to list below.

1. A. Svane and G. Santi from UAA attended the DMFT tutorial in Daresbury, June 5-6, 2003.
2. A. Svane, UAA, gave seminar in Dresden, January 8-10, 2003.
3. A. Lichtenstein, KUN, visited Paris for scientific collaboration, May , 2003.

4. A. Georges and S. Bierman, ENS-ULM, gave lectures at the DMFT tutorial in Daresbury, June 5-6, 2003.
5. G. Kotliar, RUTGERS, attended workshop of UU external team member Karlsruhe, March 31-April 1, 2003
6. A. Svane,UAA, attended workshop of UU external team member Karlsruhe, March 31-April 1, 2003
7. W. Temmerman, CCLRC, attended workshop of UU external team member Karlsruhe, March 31-April 1, 2003
8. G. Kotliar, RUTGERS, visited Paris for scientific collaboration, May, 2003
9. B. Johansson and O. Eriksson, UU, attended workshop of UU external team member Karlsruhe, March 31-April 1, 2003
10. L. Torpo, MD, visited external team member Vienna to learn the use of their VASP code, April 6-14, 2003.
11. O. Wessely and A. Grechnyev, UU, attended the DMFT tutorial in Daresbury, June 5-6, 2003.
12. J. M. O. Guillen and L. Huang, UU, attended the FPLO tutorial in Dresden, March 28-April 1, 2003.
13. M. Katsnelson, UU, visited Nijmegen for scientific exchange, May 17-24, 2003.
14. H. Winter from external team member Karlsruhe, scientific collaboration, May 12-25, 2003. D. Jervis, B. Gyorffy, J. Annett from external team member Bristol, J. Staunton and D. Rowlands from external team member Warwick, M. Foulkes from external team member IC London, and S. Stockton, C, Aerts, M. Horne and P. Strange from external team member Keele attended the Daresbury tutorial on DMFT, June 5-6, 2003. (not funded).
15. G. Santi from external team member Bristol visited Aarhus for job interview, March 2003.
16. At the Aarhus Workshop, Nov. 6-7, 2003 participated:
    a) W. M. Temmerman, Z. Szotek, M. Lüders, D. Ködderitzsch from CCLRC and I. Hughes from CCLRC external team member Warwick. The first four persons stayed until Nov. 10 for scientific collaboration (research minimeeting).
    b) I. Opahle, F. Tasnadi and M. Richter from IFW-Dresden.
    c) A. Lichtenstein and L. Pourovskii from KUN.
    d) S. Biermann from ENS-ULM.
    e) O. Eriksson, L. Nordström, B. Johansson, S. Lebegue, M. Colarieti-Tosti, N. Skorodumova, O. Bengone, A. Grechnev, T. Burkert from UU and F. Wastin, M. S. S. Brooks and J.-C. Griveau from UU external team member ITU Karlsruhe.
    f) E. Wimmer from MD.

17. At the Riksgränsen workshop, May 11-17, 2004 participated:
    a) A. Svane and G. Santi from UAA.
    b) W. M. Temmerman from CCLRC.
    c) I. Opahle and M. Richter from IFW-Dresden.
    d) M. Katsnelson, L. Pourovskii and A. Lichtenstein from KUN.
    e) M. S. S. Brooks and T. Gouder from UU external team member ITU Karlsruhe.
18. W. M. Temmerman from CCLRC visited UU May 18-20, 2004, to give a seminar and collaborative discussion.
19. M. Lüders from CCLRC visited external team member Warwick Feb. 3, 2004, participating in the workshop *Calculating* T_c *in correlated electron systems*.
20. L. Pourovskii from KUN visited UU Feb. 14-15, 2004, to participate in the workshop*Ab initio design of structural materials*.
21. L. Pourovskii, A. Lichtenstein, S. Okatov and L. Chioncel from KUN visited UU Nov. 19-21, 2003, to participate in the miniworkshop on correlated electron physics.
22. G. Santi from UAA visited CCLRC Nov. 14-15, 2004, to present a talk, and CCLRC external team member Bristol for collaborative discussionson Nov. 15-16, 2003.
23. F. Lechermann from ENS-ULM, presented his research at the '16th Annual workshop on recent Developments in Electronic Structure Methods', at RUTGERS, May 27-30, 2004.

    others:

24. Z. Szotek, G. Banach, M. Lüders, and W. Temmerman from partner CCLRC, S. Bierman, A. Georges and L. De Medici from partner ENS-ULM, G. Kotliar from partner RUTGERS, D. Koudela from partner IFW-DRESDEN and A. Lichtenstein and A. Poteryaev from partner KUN attended the Euresco conference in Trieste, Auguste 25-29, 2003.

B.5.: Training

B.5.1. The vacant Network positions have been publicised through the Psi-k Newsletter, the Psi-k mailing list and the CORDIS webpage. The Aarhus position was advertised in the 'Europhysics Journal'.

B.5.2. We encountered some initial difficulties in recruiting sufficiently well qualified PostDocs. A total of 15.5 post-doc months of training was delivered in the first year, which was clearly lower than expected. In the second year, a total of 67 post-doc months of training were delivered. At partner MD the person first employed left for another post-doc position after which the MD post-doc position was vacant for the entire second year, and a suitable candidate has just recently been found (starting Dec. 2004). Currently, 6 young researchers are employed, while three more will start around Dec. 2004, at MD, KUN and CCLRC. Thus, at the post-doc level, the Network is now fully operational.

Young researcher person-months financed by the contract						
	Contract deliverable			**Financed sofar (after 26 months)**		
Participant	Pre-doc (a)	Post-doc (b)	Total (a+b)	Pre-doc (c)	Post-doc (d)	Total (c+d)
1. UAA	0	36	36	0	17.5	17.5
2. CCLRC	0	30	30	0	21	21
3. RUTGERS	0	0	0	0	0	0
4. IFW-DRESDEN	0	30	30	0	14	14
5. KUN	0	30	30	0	15	15
6. ENS-ULM	0	30	30	0	11	11
7. UU	0	30	30	0	12	12
8. MD	0	36	36	0	5	5
Totals	0	222	**222**	0	95.5	**95.5**
First Year	0			0	16.5	16.5
Second Year	0			0	67	67
Third year, 2 mths	0			0	12	12
Third Year, all*	0			0	84.5	84.5
Total after 3 years	0	222	**222**	0	168	**168**

Table 3: Network employment of young researchers. *: first 2 months + projection for the last 10 months of year 3.

B.5.3. The network post-docs are integrated into the scientific research programme of the network by each of them being based in one of the research teams of the network partners. Each of them is taking part in one of more of the research sub-tasks of the workplan. The Network post-docs are encouraged to take active part in the Network meetings, including the tutorials, and their participation is fully financed by the Network funds.

B.5.4 All network post-docs are trained in the process of writing research articles. See the enclosed list of post-doc publications.

The post-doc participation in network meetings is summarized in section B.4.3 (post-docs are underlined). Additional post-doc training through workshop participation etc. are:

- L. Pourovskii, KUN, attended the APS march meeting in Montreal, Canada, March 21-26, 2004.
- G. Santi, UAA, gave a talk at the Aarhus workshop, entitled: *Coexistence of ferromagnetism and superconductivity in* $ZrZn_2$.
- G. Santi, UAA, attended the workshop *EXCAAR* in Aarhus, April 13-14, 2004.
- G. Santi, UAA, attended the EPS, Condensed Matter Division Conference in Prague, Czech Rep., July 19-23 2004 to give an invited talk on *Coexistence of ferromagnetism and superconductivity in* $ZrZn_2$.
- G. Santi, UAA, contributed a poster entitled *Ab-initio calculations of the electronic structure and superconducting properties of* $PuCoGa_5$ at the Workshop of the Danish Center for Scientific Computing, Odense Sept. 15 2004.
- M. Lüders, CCLRC, gave a talk at the Aarhus workshop, entitled: *Local self-interaction correction in the KKR method.*
- M. Lüders, CCLRC, gave a talk on *The local SIC method* at a KKR meeting in Munich, Feb. 13-15, 2004.
- M. Lüders, CCLRC, attended a Shared Memory programming course in Edinburgh, Apr. 4-5, 2004.
- M. Lüders, CCLRC, on a training visit to Freie Universität Berlin, May 11-16, 2004.
- M. Lüders, CCLRC, presented the group's work at the EuroCORES meeting in Lancaster, May 20-21, 2004.
- M. Lüders, CCLRC, presented a poster at the workshop 'Beyond DFT' in Leiden, July 11-17, 2004.
- M. Lüders, CCLRC, took part in the writing of a EU-proposal for an I^3 infrastructure in electronic structure calculations.
- M. Lüders, CCLRC, is the band-structure-theory group's e-science representative in the Daresbury e-Science Committee.

- F. Tasnadi, IFW-DRESDEN, attended the workshop 'School on nanostructured systems: Basic Properties and Technology', in Bedlewo, Poland, May 11- June 2, 2004.
- S. Lebegue, UU, visited Los Alamos, USA, June 5-19, 2004 on a collaborative visit.

Two post-doc travels to USA, F. Lechermann's to RUTGERS mentioned in Section B.4.3, and L. Pourovskii's to the APS meeting, mentioned above, were financed with Network money after approval of the Commission. S. Lebegue's travel to Los Alamos was financed by other sources. A travel of F. Tasnadi to UC Davis, California was cancelled due to visa problems.

During the reporting period the Network has organised a hands-on-course on the FPLO software package specifically aimed at training young researchers in the methodology of the field. Likewise, a tutorial meeting has been held on the formalism of the Dynamical Mean Field theory. Several tutorials are planned for 2005.

The UU post-doc, S. Lebegue, was trained in the practical aspects of workshop organisation, as he handled most of the practical matters in connection with the Riksgränsen workshop. Likewise, the IFW-DRESDEN post-doc, F. Tasnadi, took part in the organisation of the *Hands-on FPLO* workshop organised by the Dresden group at UC Davis.

All network post-docs have been encouraged to create their personal homepage as part of establishing them-selves in the community of electronic structure theoreticians.

F. Tasnadi, DRESDEN post-doc, has given a practice seminar at TU-Dresden.

G. Santi, UAA post-doc, has followed a language course in Danish.

B.5.5. No special measures have been taken to promote equal opportunities.

B.5.6. The research of the Network naturally involves multidisciplinarity, as it belongs to the border region of physics and chemistry with the basic tools being those of large software packages and supercomputers. The training in computer skills including various sorts of practical issues like data storage management, computer resource allocation and internet based communications (such as grid conferencing) and information retrieval is at the heart of the matter.

B.5.7. The industrial partner MD has been training one post-doc for 5 months, but did not provide any training in the past year, as a suitable candidate for the vacant position was difficult to find. A fair number of candidates expressed interest but had to be turned down due to conflict with the age and nationality requirements. In the spring 2004 a suitable person was found, starting Dec. 2004.

The MD scientist-in-charge, Erich Wimmer gave a seminar at the Aarhus workshop entitled *Industrial Aspects in the Use of f-electron Solids.* Partner MD is coorganising the 2nd annual network meeting in Paris, Dec. 2004.

A special workshop addressing the Industrial aspects of our research is scheduled for 2006.

The Paris node collaborates with the CEA ("Commissariat a l'energie atomique").

The Nijmegen node collaborates with researchers at Siemens on a project of rare-earth impurities in half-metallic systems.

B.6.: Difficulties

In the first year of Network operation we encountered some difficulty with the recruitment of young researchers. It took 12 months to reach the level of full operation.

The only significant difficulty in the second year of Network operation has been the recruitment of a suitable post-doc at partner MD. This problem is now solved.

PART C - FACTUAL INFORMATION ON THE YOUNG RESEARCHERS

Name	Nationality	Age	Start Date	End Date	Speciality
Leena Torpo	**FIN**	31	1/2/03	31/06/03	P-10, P-11
Martin Lüders	**D**	35	1/2/03	31/1/05	P-10, P-13
Gilles Santi	**CH**	33	15/5/03	14/5/05	P-10, P-13
Leonid Pourovskii	**RU**	28	1/8/03	31/7/05	P-10
Ferenc Tasnadi	**HU**	28	1/9/03	31/8/05	P-10, P-12
Sebastien Lebegue	**F**	26	1/11/03	31/10/05	P-10, P-11
Frank Lechermann	**D**	29	1/12/03	30/09/05	P-10
Diemo Ködderitzsch	**D**	31	1/12/04	31/1/05	P-10
Alexei Griechnev	**UA**	28	1/12/04	31/5/06	P-10
Rene Windiks	**D**	33	1/12/04	31/5/06	P-10

Table 4: List of Young Researchers. All are post-doc's.

.

Name	Place of work	Country	Prev. with other partner
Leena Torpo	MD, LeMans	**F**	-
Martin Lüders	CCLRC, Daresbury	**UK**	CCLRC
Gilles Santi	UAA, Aarhus	**DK**	CCLRC(Bristol)
Leonid Pourovskii	KUN, Nijmegen	**NL**	-
Ferenc Tasnadi	IFW-DRESDEN	**D**	Dresden
Sebastien Lebegue	UU, Uppsala	**S**	-
Frank Lechermann	ENS-ULM, Paris	**F**	-
Diemo Ködderitzsch	CCLRC, Daresbury	**UK**	CCLRC
Alexei Griechnev	KUN, Nijmegen	**NL**	UU
Rene Windiks	MD, LeMans	**F**	-

Table 5: Working place of Young Researchers.

4 News from the ESF Programme

”Towards Atomistic Materials Design”

4.1 Reports on ESF Workshops/Conferences

4.1.1 Report on Psi-k/CECAM Workshop

Scientific Report of the Workshop
on
”The Nature of Hydrogen Bonding and Density Functional Theory”

CECAM in Lyon, France, in June 2-5

Summary:

This workshop brought together the key theoreticians who have analyzed the nature of hydrogen bonding (hbs) and the quality of exchange-correlation functionals in Density Functional Theory (DFT) for describing them. The main objective of the workshop was to discuss about the accuracy of different exchange-correlation functionals to predict hb interactions, i.e. hb strength and geometry, hb cooperativity, phonon frequencies, and proton transfer barriers in hydrogen bonded systems. The goal was successfully attained. The broad importance of hbs in diverse fields was reflected by the participation of 48 scientists from biological, chemical, and physical fields, including the Novel Prize in chemistry, Professor Walter Kohn, founder of DFT.

Invited and contributed presentations confirmed that DFT-GGA often does describe hb systems well. However, it was also stressed that hb’s are actuated by both, ionic and dispersion interactions. Because the latter are absent in DFT-GGA the description becomes inaccurate when the hb geometry deviates from a linear arrangement. Furthermore it was noted that utmost care must be taken with other sources of errors, e.g. basis sets or numerical parameters of the simulations. Also it was shown that DFT is the method of choice for treating complex hb systems with acceptable accuracy nowadays, except when van der Waals interactions become important for the description of the system. Therefore the development of new xc-functionals for a proper treatment of van der Waals interactions is needed. When this inclusion is done properly it will also improve the accuracy for describing hbs. For such direction some promising results were presented in this workshop.

The workshop consisted of 20 invited talks (see the below table), 20 posters (see the poster abstracts below), and ample time for discussion.

	Joel Ireta	ireta@fhi-berlin.mpg.de
Organisers:	Martin Fuchs	fuchs@fhi-berlin.mpg.de
	Matthias Scheffler	scheffler@fhi-berlin.mpg.de

Invited Speakers:

Baerends EJ	Vrije Universiteit, Amsterdam, The Netherlands
Dixon DA	University of Alabama. Tuscaloosa, USA
Elstner M	Universitaet Paderborn, Paderborn Germany
Fuchs M	Fritz-Haber-Institut, Berlin Germany
Galli G	Lawrence Livermore National Laboratory, USA
Guo H	University of Tennessee, Knoxville USA
Hobza P	Academy od Sciences of the Czech Republic, Prage, Czech Republic
Jalkanen KJ	Technical University of Denmark, Lyngby, Denmark
Kohn W	University of California, Santa Barbara, USA
Laasonen K	University of Oulu, Oulu, Finland
Marx D	Ruhr-Universitaet Bochum Germany
Müller-Dethlefs K	University of York, York, UK
Raugei S	SISSA, Trieste, Italy
Salahub DR	University of Calgary, Calgary, Canada
Sauer J	Humboldt-Universitaet, Berlin, Germany
Savin A	CNRS et Universite Paris VI, Paris, France
Senet P	Universite de Bourgogne, Dijon, France
Scuseria G	Rice University, Houston, USA
VandeVondele J	University of Cambridge, Cambridge, UK
Yang W	Duke University, Durham, USA

Program:

June 2

14:00-14:50		Registration
14:50-15:00	M. Scheffler	Welcome
15:00-15:45	D. R. Salahub	Towards an accurate description of hydrogen bonds in complex environments
15:45-16:30	M. Elstner	Studying H-bonded systems and proton transfer reactions with DFT and approximate DFT methods
16:30-17:00		Coffee and Discussion
17:00-17:45	G. Scuseria	Benchmarking recent DFT functionals on hydrogen-bonded systems
17:45-18:30	W. Kohn	Van der Waals attractions between systems of arbitrary size and shape

June 3

9:30-10:15	P. Hobza	Molecular interactions in DNA and proteins: success and failure of DFT
10:15-11:00	J. Sauer	Hydrogen bonds in the gas phase and in solids. DFT and beyond DFT
11:00-11:30		Coffee and Discussioni
11:30-12:15	D. A. Dixon	Free energies of solvation based on molecular clusters
12:15-13:00	K Müller-Dethlefs	Competition between van der Waals and hydrogen bonding: the phenol-argon2 cluster
13:00-14:30		Lunch
14:30-15:15	A. Savin	Electronic space sharing
15:15-16:00	W. Yang	(1) Potential functionals – dual to density functionals and solution to the v-representability problem. (2) Critical role of the hydrogen bond of a water molecule in the catalysis of 4–oxalocrotonate tautomerase
16:00-16:30		Coffee and Discussion
16:30-19:00	Poster Session and Buffet	

June 4

9:30-10:15	E. J. Baerends	Car-Parrinello MD study of the role of hydrogen bonds in the Fenton reaction
10:15-11:00	K. J. Laasonen	AIMD simulations of very high concentration acids, water in very ionic environment
11:00-11:30		Coffee and Discussion
11:30-12:15	J. VandeVondele	Ab initio molecular dynamics simulations of liquidi water: an update
12:15-13:00	S. Raugei	Path integral simulations and the role of nuclear quantum effects in water and HF
13:00-14:30		Lunch
14:30-15:15	G. Galli	Ab-initio simulations of water and simple aqueous solutions
15:15-16:00	D. Marx	”Difficult” hydrogen bonds: Solvating OH and dealing with ammonia
16:00-16:30		Coffee and Discussion
16:30-17:15	H. Guo	Understanding the nature and role of hydrogen bonding during biological function from QM/MM studies
17:15-18:00	P. Senet	Ab initio studies of charge distributions and dielectric properties of water clusters and of water-protein bond
19:00		Conference dinner

June 5

9:30-10:15	M. Fuchs	Diffusion monte carlo study of hydrogen bonded model systems
10:15-11:30	K. Jalkanen	Hydrogen bonding effects observed via vibrational absorption, vibrational circular dichroism, Raman scattering and Raman optical activity spectroscopy: a marriage between experiment and theory
11:30-12:00		Coffee and Discussion

Abstracts:

DFT description of van der Waals forces with explicit long-range interactions

János G. Ángyán, Iann Gerber
Laboratoire de Cristallographie et de Modélisation des Matériaux Minéraux et Biologiques
CNRS - Université Henri Poincaré Vandœvre-lés-Nancy, France
Andreas Savin, Julien Toulouse
Laboratoire de Chimie théorique CNRS-Université Paris VI Paris, France

Dispersion (van der Waals) forces are due to long-range electron correlation effects that are notoriously absent from local and semi-local density functionals leading to an incorrect asymptotic behaviour of the interaction energy between non-polar systems. Moreover, the region of van der Waals minimum is described by most of the current functionals in a rather erratic manner: LDA strongly overbinds, some GGA functionals lead to repulsive interaction potentials, others succeed in predicting a minimum but with an unreliable well depth. The separation of electron-electron interactions to short- and long-range components provides a satisfactory framework for treating both of the above-mentioned problems. Short-range exchange and correlation effects are continued to be described by appropriate density functionals, while long-range electron interactions, exchange and correlation, are handled explicitly. A perturbational solution for the resulting effective Schrödinger equation is proposed. A possible choice for the zeroth order problem leads to a novel kind of hybrid functional, where the short-range exchange-correlation functional is combined with a long-range exact-exchange. As expected, this "range-separated" hybrid functional leads to a repulsive van der Waals interaction potential for rare gas dimers. By adding explicit MP2-like long-range electron correlation corrections, one obtains an asymptotically correct seamless energy expression, that is not dependent by any explicit partitioning of the system to interacting parts.

Importance of non-covalent interactions in the internal rotation around the C-N bond in 3-(o-aryl)-5-methyl-rhodanines

Yeliz Aydeniz, Funda Oğuz, Arzu Yaman, Aylin Sungur Konuklar, Ilknur Doğan, and Viktorya Aviyente
Department of Chemistry, Boğazici University, Bebek, Istanbul
Roger A Klein
Institute for Physiological Chemistry, University of Bonn, Germany

Thiazolidinediones and rhodanines are known to possess pharmacological activity[1] and to be very effective in improving glycaemic control in diabetic patients, potentiating the action of insulin and thus lowering blood glucose levels. Rhodanines have both antiviral and antibacterial activity.[2] We have investigated the pairs of rotational isomers for six 3-(o-aryl)-5-methyl-rhodanines (X = H, F, Cl, Br, OH, and CH3) using NMR spectroscopy and density functional theory (DFT) calculations. Electron density topological and NBO analysis has demonstrated the importance of non-covalent interactions, characterised by (3,-1) bond critical points (BCPs), between the oxygen and sulphur atoms on the thiazolidine ring with the aryl substitutents in stabilising the transition states. Rotational barriers for 3-(o-chlorophenyl)-5-methyl-rhodanine and 3-(o-tolyl)-5-methyl-rhodanine were determined experimentally based on NMR separation of the diastereoisomeric enantiomeric pairs, and the first-order rate constants used to derive the value of the rotational barrier from the Eyring equation. The effect of hydrogen bonding in stabilising the transition structures is discussed where present.

1. B.C.C. Contello, M.A. Cawhorne, D. Haigh, R.M. Hindley, S.A. Smith and P.L. Thurlby. Bioorg. Med. Chem. Lett., 1994, 4, 1181-1184.
2. B.C.C. Contello, D.S. Eggleston, D. Haigh, R.C. Haltiwanger, C.M. Heath, R.M. Hindley, K.R. Jennings, J.T. Sime and S.R. Woroneicki. J.Chem. Soc. Perkin Trans. 1994, 1, 3319-3324.

Hydrogen bonded water in zeolite

L. Benco[a,b], T. Bucko[a], J. Hafner[a]
[a]*Institute for Materials Physics, Vienna University, A-1090 Vienna Austria*
[b]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia*

Zeolies are microporous materials used as industrial catalysts. The famework Al/Si substitutions of zeolite structures are compensated by extra-framework cations. Such cations are easily converted to the H-form. The hydrogen atom, bound to the framework O-atom, represents an active center of the zeolite, called Brønsted acid site. Figure below (left) shows an example of the adsorption of water on the Brønsted acid site. Upon adsorption a series of distinct O-H stretching frequencies appears in the IR spectrum, known as ABC triplet (cf. Figure, center). The features of the IR spectrum, that are rather independent of the zeolite framework, were investigated by various theoretical approaches, but still have not been satisfactorily assigned [1,2]. Right panel of Figure shows the three O-H stretching frequencies calculated as Fourier transform of the atomic velocity autocorrelation function of one water molecule adsorbed on the Brønsted acid site in mordenite using the PW91 functional. All three calculated frequencies (1-3) reasonably fit the experimental curve [3,4]. The frequency of atom 1 seemingly corresponds with the band C, but there is no explanation for the origin of the bands A and B. Both bands are situated on the steep part of the dependence where a small change in the interatomic distance causes a large change of the O-H stretching frequency. Are geometries calculated with PW91 wrong to such an extent, that circumvent understanding of simple spectra. We look for the answer to this question comparing geometries and frequencies for various functionals including PW91, PBE and RPBE.

1. M. Krossner, J. Sauer, J. Phys. Chem. 100 (1996) 6199.
2. V. Termath, F. Haase, J. Sauer, J. Hütter, M. Parinello, J. Am. Chem. Soc. 120 (1998) 88512.
3. L. Novak, In Strucure and Bonding, Vol. 18, J. D. Dunitz, Ed., Springer, Berlin, 1974, p. 177.
4. E. Libowitzky, Monatshefte für Chemie 130 (1999) 1047.

Proton transfer under high pressure

Martine Castellà-Ventura, Mari-Hélène Limage and François Fillaux
LADIR/CNRS and UPMC, 2 Rue Henri Dunant, 94320 - Thiais

Proton transfer dynamics along hydrogen bonds in the quantum regime depends on the chemical nature of donor and acceptor, on the distances between the two proton sites, and on the shap e of the potential function. It is governed by a double minimum potential along the reactio n path, characterized by the barrier height, the distance between the two minima, and the energy difference between the two wells or potential asymmetry. A way to investigate the proton transfer dynamics as a function of the potential shape is to study a lot of samples, with hydrogen bonds of different strength. A much more convenient approach consists in applying a pressure to a single sample. At very high pressures, the hydrogen bond is strengthened and the proton transfer dynamics is modified. The barrier height, the distance between the two wells and the energy difference between the two minima decrease. This is the so-called ”symmetrization” phenomenon.

This dynamics can be observed by infrared and Raman spectroscopies. Very high pressures can be obtained with diamond anvil cell.

Potassium hydrogenocarbonate $KHCO_3$ is a prototypical system, which contains centro-symmetric dimer entities linked by moderately strong hydrogen bonds (2.587 Å), with quasi-symmetric double minimum potential at ambient pressure.[1] This effective potential describes the quantum transfer of a single proton along a straight line.

The main results are the following ones. Below 40 GPa, phenomena are reversible. Three ranges corresponding to spectral discontinuities (> 1.8 GPa, 4-5 GPa and 20-25 GPa) can be distinguished. They are likely due to phase transitions. The $\nu(OH)\cdots O$ frequency increases from 214 cm^{-1} at atmospheric pressure to 330 cm^{-1} at 40 GPa. This reveals a large decrease of the $O\cdots O$ distance. These observations suggest a symmetrization process.

The behavior of $KHC0_3$ under high pressure is compared to that of another system, the potassium maleate $KH(COOCH)_2$. This compound contains intramolecular strong hydrogen bonds

(2.437 Å), with single minimum potential at ambient pressure.[2]

1. F. Fillaux, Chem. Phys. 74 (1983) 405.
2. F. Fillaux, N. Leygue, J. Tomkinson, A. Cousson, W. Paulus, Chem. Phys. 244 (1999) 387.

A dynamical study of the effect of water molecules on the structure of Cu-zeolites

A. Goursot, D. Berthomieu
LMCCCO UMR-CNRS 5618, ENSCM, 8 Rue de l'Ecole Normale, 34296 Montpellier Cédex 5, France
S. Krishnamurty
Department of Theoretical Chemistry, National Chemical Laboratory Pune 411008, India

Copper ions exchanged in ZSM-5, FAU or beta zeolites are used to catalyze deNOx decomposition, which involves the presence of water as reaction product, leading to hydration of the copper ions and changes of the active sites. Moreover, the flexibility of the zeolite frameworks is also a well-established property, leading to the idea that this flexibility is necessary for the catalytic reactions to occur, the surface of the material changing upon adsorption of reactants and, most probably, during the reaction.

These dynamical changes, that may occur at the active catalytic sites, are thus quite important to model, if one wants to understand the intermediate steps of a reaction.

Born-Oppenheimer molecular dynamics simulations have been performed on models of Cu(I) and Cu(II)-FAU zeolite in the presence of H2O molecules. They show that only average binding energies and coordination should be considered for the metal-zeolite and metal-adsorbents binding.

Our calculations show that, in general, the metal-zeolite bonding decreases in the presence of water, leading to a more exposed Cu ion, which provides a kind of "homogeneous" catalytic environment. We found no evidence for full hydration of Cu(II) cations which would be accompanied by a migration to other sites. However, this process occurs when Cu(II) is reduced to Cu(I) in the presence of water molecules.

Ultrafast dissociation of adenine:water hydrogen bonds by photoexcitation

Myrta Gruning, Alberto Castro, Angel Rubio

Recent molecular-beam studies of hydrated cluster of adenines show the anomalous loss of the solvent molecules after excitation by a femtosecond laser pulse at 262 nm(1). The goal of this work is to provide the molecular mechanism behind this phenomenon working within the time-dependent density functional theory (DFT) framework.

The dissociation of the hydrogen bonds has been attributed to the dissociative character of the potential energy surface in the excited state: we investigate this hypothesys by calculating the evolution of the system after the interaction with the laser pulse with real-space real-time time dependent DFT. Preliminary results will be presented.

These calculations pose several problems that are rather challenging for the present exchange-correlation functionals: which is the preferred hydrogen bonding site, the description along the adenine-water hydrogen bond coordinate of the potential energy surfaces of the involved excited states, the water-water .vs. water-adenine interaction.

1. Kang et al. Chem. Phys. Lett. (2002) 359, 213; Kim et al. J. Phys. Chem. A (2000) 104, 6552.

Hydrogen bond strength in left-handed helices

Franziska Grzegorzewski, Joel Ireta and Matthias Scheffler
Fritz Haber-Institut der Max Planck-Gesellschaft, Faradayweg 4-6, D- 14 195 Berlin-Dahlem, Germany

The right-handed α-helix is the most ubiquitious structural motif in globular proteins, and understanding its properties is crucial to understanding protein folding. However, left-handed helices are rarely found in nature. The common explanation is that side groups disfavor the left-handed enantiomer due to a steric effect.

In order to gain a deeper understanding of how the handedness affects the helical stability we studied the energetical and vibrational properties of an infinite polyalanine chain in a left-handed 3_{10} and α-helical conformation by using density functional theory. The study was carried out exploiting periodic boundary conditions and ab initio pseudopotentials, together with the Perdew-Burke-Ernzerhof generalized gradient approximation to the exchange-correlation functional. The calculated results were compared to previous theoretical investigations on right-handed polyalanine systems in 3_{10} and α-helical structure.

We demonstrate that the right-handed helix is only stabilized by 1 kcal/mol over the left-handed isomer. Hence both structures are stable with respect to the fully extended system. In addition we determine the strength of the steric effect and assign it to the interactions between the carbonyl group of the helix backbone and the lateral group.

As the major result of our calculations we show that there are significant differences between the hydrogen bond strength in the enantiomeric conformations. Thus surprisingly hydrogen bonds are about 9% stronger in the left-handed conformation, leading to a more compact equilibrium structure.

Hydrogen bonding in water studied by x-ray Compton scattering

M. Hakala, K. Nygård, K. Hämäläinen, S. Manninen
Division of X-ray Physics, University of Helsinki, Finland
S. Huotari
European Synchrotron Radiation Facility, France
Ph. Wernet
BESSY, Germany
A. Nilsson
Stanford Synchrotron Radiation Laboratory, USA
L.G.M. Pettersson
University of Stockholm, Sweden

We study hydrogen bonding and coordination properties of water molecules using x-ray Compton scattering (inelastic x-ray scattering at high energy and momentum transfers) [1]. In x-ray Compton scattering the scattering cross section is, within the impulse approximation, proportional to the so-called Compton profile. Compton profile is a plane integral of the momentum density of the system and can be modeled by calculations based on the density-functional theory (GGA functionals, Gaussian type basis functions). From our model calculations using clusters of water molecules we obtain the fingerprint of the hydrogen bond in the Compton profile. The main effect in the Compton profile upon the H-bond formation follows from the exchange interaction between the overlapping orbitals of the neighboring molecules. The effect of intramolecular polarization is weak, whereas charge transfer modifies the profile. The signal of the hydrogen bond is also sensitive to the bond length. Our theoretical predictions suggest that x-ray Compton scattering is potentially an important complementary method to study the nature of the hydrogen bond in different systems. We will also present preliminary experimental results on water (experiments performed at European Synchrotron Radiation Facility, France).

1. M. Hakala, S. Huotari, K. Hämäläinen, S. Manninen, Ph. Wernet, A. Nilsson, L.G.M. Pettersson, submitted to Phys. Rev. B

A DFT investigation into the inhibition of cyclin dependent kinases

L. C. Heady

Cyclin-dependent kinases (CDKs) are a group of proteins which are responsible for controlling entry to the different phases of the cell cycle, and are therefore promising targets for the treatment of cancerous tumours. Using linear scaling DFT techniques, benchmarked against parameter-free plane-wave techniques we have calculated the binding energy of a number of different inhibitors to the ATP binding pocket of CDK2. Particular attention has been paid to the convergence of the binding energy with respect to system size. Differences in solvation energy between inhibitors have been calculated within the Generalised Born Approximation. The binding energies calculated predict the correct rank order of the inhibitors considered and correlate well with the available experimental values of binding affinity. We find that the dominant interactions in the pocket are the direct hydrogen bonds between the inhibitors and the peptide backbone. Therefore, accurate measurements of the hydrogen bond strength are needed to understand the subtle differences in chemical affinity of different inhibitors for CDK2. The effect of the presence of water molecules in the binding pocket has been investigated in a series of classical molecular dynamics simulations with explicit solvent. These correctly reproduce the positions of most of the water molecules present in the available crystallographic structures. Comparison between CDK2 and a mutated structure that mimics the binding site of CDK4 shows very similar hydrogen bonded networks of water molecules within the binding pockets. This suggests that the two pockets will form hydrogen bonds to inhibitors in an analogous way. Further investigations will look at how the strength of these hydrogen bonds is modulated by their different chemical environments.

First principles vibrational and thermodynamic analysis of the secondary structure of proteins

L. Ismer, J. Ireta, and J. Neugebauer
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

For a detailed understanding of the functionality of proteins an accurate description of their dynamical properties is crucial. For example, characteristic fingerprints in the vibrational spectrum allow the identification of specific secondary structural elements in the protein (such as e.g. an α-helix, a β-sheet or a γ-turn) via spectroscopic methods. Further, particularly the lower frequency vibrational branches strongly determine the thermodynamic stability (free energy) of the secondary structure and affect conformational fluctuation processes of biological importance (e.g. protein folding). A key interaction for the stability of the secondary structure is intra-chain hydrogen bonding. A problem in describing hydrogen bonds is that due to their polar nature they strongly interact with each other [1] – realistic models for the secondary structure must take cooperativity into account. We have therefore performed a harmonic vibrational analysis on an infinite α-helical secondary structure motif by employing DFT-GGA. The major advantages compared to previously performed empirical force field studies are that cooperative effects are fully taken into account and that our results are free of any experimental input parameters, thus allowing for reasonable predictions also away from experimentally obtainable parts of the vibrational spectrum.

Our calculated phonon dispersion relation of the polyalanine α-helix showed excellent agreement with experimentally available data [2]. In comparison to previous works, based on force fields which were optimized to fit the experimental data, we observe a significant blue shift by up to 40 cm^{-1} for the two lowest lying branches, i.e. the acoustical branches. Our results show that a likely mechanism to explain this shifting is hydrogen bond cooperativity, i.e. accounting for this effect is crucial to obtain accurate acoustical branches [3]. Since the low frequency branches dominate the vibrational entropy and the low temperature heat capacity, we further checked whether our results lead to changes in these quantities. Indeed, a comparison to available experimental data [4] yielded a significant improvement with respect to force field results for the specific heat at temperatures below 150 Kelvin.

Further, we performed a comparative study of the α-helix against a reference system, where hydrogen bonds are completely absent, i.e the flat, fully extended conformation (FES), and found that the low frequency branches of the FES are significantly red-shifted. A thermodynamic analysis revealed that this red-shifting lowers the stability of the α-helix with respect to the FES by about 0.8 kcal/mol at 298K due to vibrational contributions to the free energy. However due to its much larger electronic stability of 2.7 kcal/mol [1], caused by the hydrogen bond formation, the α-helix is still stable against the FES by 1.9 kcal/mol at 298K.

1. J. Ireta, J. Neugebauer, M. Scheffler, A. Rojo, and M. Galvan, J. Phys. Chem. B, 107:1432, 2003
2. S.H. Lee and S. Krimm, Biopolymers, 46:283, 1998
3. L. Ismer, J. Ireta, S. Boeck, and J. Neugebauer, submitted to Phys. Rev. Lett.
4. M. Daurel, P. Delhaes, and E. Dupart, Biopolymers 14:801, 1975

First principles NMR indirect spin-spin coupling calculations of hydrogen-bonded molecular crystals

S. Joyce, J. Yates, C. Pickard, M. Payne
Theory of Condensed Matter, Cavendish Laboratory, Cambridge.
F. Mauri
Laboratoire de Mineralogie-Cristallographie de Paris, Universite Pierre at Marie Curie.

We have recently developed an all-electron theory for the calculation of NMR indirect spin-spin coupling in periodic systems. Traditionally, spin-spin coupling calculations have been confined to molecules and finite clusters. However, our method is the first to be formulated for extended periodic systems. This broadens the range of systems that can be investigated computationally and has resulted in many varied and important potential applications. Through-out the years, spin-spin coupling measurements have only been used in conjunction with NMR chemical shifts. Nevertheless, recent improvements in experimental techniques have shown spin-spin coupling to be an indespensible tool in its own right, particularly as a direct measure of the presence of hydrogen bonding. Here we present our solid-state method applied to hydrogen bonded molecular crystals.

Structural and computational studies of amino acids

P. Lozano-Casal, D. R. Allan, S. Parsons, and C.Morrison
School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh.

The study at high pressures of biologically important compounds, for example, amino acids, proteins and enzymes has until relatively recently been largely neglected, although their structure, functionality and behaviour is fundamental over all species, from bacteria to human being. The knowledge of how these compounds are affected by changing the pressure in their environment is crucial to the understanding of the existence of life at extreme conditions, for example life in the deep ocean, where the pressure is about 1200 times that on the surface. This work would also be pivotal to our knowledge of the synthesis of biological molecules at high pressures, which would be important for the Biological Sciences and our understanding of how life begun. However, the study of these systems at high pressure is not straightforward and the standard techniques for probing molecular structure, such as X-ray and Neutron diffraction with single crystals and powders, and IR and Raman Spectroscopy among others must be adapted for high-pressure work. More recently, advances in computer simulation techniques allow calculations that can complement the experimental results and provide structural information that is not accessible with experimental techniques.

We have recently explored the behaviour of some amino acid crystal structures at high pressure using single crystal X-ray diffraction techniques and ab initio calculations. Pressure can induce conformational changes and structural phase transitions in the crystal structures of small molecules. We are extending this work to simple biological molecules particularly the amino acids.

We have been working, principally, with L-α-glutamine and L-α-asparagine monohydrate, which crystallises in the orthorhombic system at ambient conditions. It was found that by applying pressure the cell parameters were reduced and the intermolecular donor-H-acceptor interactions were shortened but with no structural phase transition up to the pressure of 45-49kbar.

In addition, computational studies have shown that it is possible to locate hydrogen atoms that the experimental technique could not find and that it is possible to obtain the sublimation, lattice and proton transfer energies, together with the energy of the hydrogen bonding.

Finally, the relationship between the strength of the hydrogen bonding and the compressibility caused by an increment of the pressure has been studied for both systems in order to find trends in their behaviour.

Glycine on a wet pyrite surface at extreme conditions

Christian Boehme, Eduard Schreiner, Rodolphe Pollet and Dominik Marx
Lehrstuhl fuer Theoretische Chemie, Ruhr-Universitaet Bochum, 44780 Bochum, Germany

The recently proposed "iron-sulfur world" (ISW) scenario [1] is an intriguing contribution to the controversial field of "Origin of Life" research. At the very heart of the ISW is the idea that prebiotic chemistry might have taken place near deep sea volcanoes (hydrothermal vents) at extremely high pressures and temperatures. In particular, the interface between hot pressurized water and Fe/S minerals, such as pyrite, is crucial to this scenario. A key step for building proteins is the formation of the peptide bond. It has been demonstrated that this reaction, which is usually unfavorable in water, can be carried out in the presence of FeS, H2S, and CO in aqueous solution at elevated temperature and pressure [2]. While this is a major success for the ISW, the mechanism of this unusual reaction is not yet understood.

Furthermore, pressure and temperature of this experiment were much lower than the ISW requires. In an effort to contribute to this discussion we present ab initio molecular dynamics (MD) simulations [3,4] of the simplest amino acid, glycine at the pyrite/water interface under ISW conditions. Our aim is to understand the very first step of pyrite-assisted peptide bond formation, which is the adsorption of gly on the pyrite surface and its possible activation. The results are not only interesting in the context of the ISW, but also explore unusual chemistry [5]. The simulations show that Gly bound by one carboxylate oxygen and the ammonium group easily desorbs from a pyrite/water interface, while the retention time of gly bound by both carboxylate oxygens is much longer. The desorption process is water-assisted, and the surface bonding is best understood as an electrostatic interaction. We have also found indications of a Gly activation due to the interaction with the surface. This might open an avenue into the experimentally observed peptidization and is the subject of ongoing research.

1. Waechtershaeuser, G. Prog. Biophys. molec. Biol. 1992, 58, 85 201.
2. Huber, C.; Waechtershaeuser, G. Science 1998, 281, 670 672.
3. Car, R.; Parrinello, M. Phys. Rev. Lett. 1985, 55, 2471 2474.
4. Marx, D.; Hutter, J. Ab initio molecular dynamics: Theory and Implementation. In Modern Methods and Algorithms of Quantum Chemistry, Vol. 1; Grotendorst, J., Ed.; NIC: Juelich, 2000 http://www.theochem.rub.de/go/cprev.html.
5. Boehme, C.; Marx, D., J. Am. Chem. Soc.2003, 125, 13362 - 13363.

Influence of stacking upon the hydrogen bonding capacity of aromatic nitrogen. The use of DFT based reactivity indices in the prediction of the stacking interaction

Pierre Mignon, Goedele Roos, Stefan Loverix, Paul Geerlings
Eenheid Algemene Chemie (ALGC), Faculteit Wetenschappen, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium
Stefan Loverix
Dienst Ultrastruktuur, VIB (Vlaams Interuniversitair Instituut Biotechnologie), Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

The influence of stacking upon the ability of an aromatic nitrogen atom to accept a hydrogen bond is investigated. Calculations at the MP2/6-31G(0.25)[1] level were carried out for ten complexes between substituted benzenes and pyridine stacked in the parallel offset conformation. The interaction energy between pyridine and the substituted benzenes is analysed in terms of HF, correlation and electrostatic contributions. It appears that the nitrogen proton affinity (calculated as the minimum of the Molecular Electrostatic Potential[2]) is directly related to the charge transfer to the pyridine and to the hardness of the substituted benzenes. We observe also that DFT based descriptors[3] such as the local hardness, and benzene ring polarisability are good tools to predict the interaction energy. Finally the nitrogen hydrogen bonding ability of the pyridine is directly related to the electrostatic interaction between the cycles. This finding may be important in the study of DNA/RNA chains.

1. Hobza, P.; Sponer, J. Chemical Reviews 1999, 99, 3247-3276.
2. Baeten, A.; De Proft, F.; Geerlings, P. International Journal of Quantum Chemistry 1996, 60, 931-940.
3. Geerlings, P.; De Proft, F.; Langenaeker, W. Chemical Reviews, 2003, 103, 1793-1873.

Hydrogen bonds in the activation of electrophile and nucleophile in the Michaelis complex of arsenate reductase

G. Roos[a], J. Messens[b], S. Loverix[a,b], L. Wyns[a] and P. Geerlings[a].
[a] *Vrije Universiteit Brussel (VUB), Eenheid Algemene Scheikunde (ALGC), Pleinlaan 2, B-1050, Brussels, Belgium.*
[b] *Vrije Universiteit Brussel (VUB), Dienst Ultrastructuur, Vlaams interuniversitair Instituut voor Biotechnologie (VIB), Pleinlaan 2, B-1050, Brussels, Belgium.*

Arsenate reductase (ArsC) catalyses the reduction of arsenate to arsenite in a multistep mechanism. The first step involves the nucleophilic attack of a cystein thiolate (Cys10) on the arsenic

atom leading to a covalent sulfur-arseno intermediate[1]. At the optimum pH for enzymatic catalysis of ArsC (pH = 8.0)[2], a substantial amount of free cysteine (pK_a = 8.3) is present in the thiolate form. Apart from the backbone amide hydrogens of Gly12 and Asn13, Ser17 is the only residue that interacts directly with Cys10[3]. Since Ser17 can not function as a general base we strongly suggest nucleophilic catalysis with a stabilized thiolate form in the reactant state. Hydrogen bonds are known to have a pK_a lowering effect on the acceptor molecule, especially when the donor molecule is positively charged[4]. However, this is not the case for the Cys10Sγ–H-OγSer17 hydrogen bond in pI258 ArsC and as such this single interaction is unlikely to suppress the pK_a of Cys10 sufficiently. But the presence of a K^+-Cys10 hydrogenbond interaction network via Asn13 and Ser17 activates the nucleophile, the thiolate species of Cys10 by sufficiently lowering its pK_a to 6.7[ref.5].

The hydrogen bond from Arg16 to the leaving hydroxyl group of arsenate and the hydrogen bonds from various backbone amide nitrogens of the catalytic site to the other oxygen atoms of arsenate account for an increased electrophilicity of the central arsenic atom. Especially Arg16 is identified as groundstate destabilizator[5].

The second step in the reaction mechanism catalysed by ArsC involves the nucleophilic attack of Cys82 on the sulfur-arseno adduct. Cys82 is activated by two strong hydrogen bonds from Thr11 to Cys82, which increases the nucleophilicity of the attacking centre, SγCys82.

All calculations are performed onusing the B3LYP functional in a 6-31+G** basis set[6].

1. a) Zegers I., Martins J.C., Willem R.,Wyns L., Messens J., Nature Struct. Biol. 2001, 8, 843. b) Messens J., Martins J.C., Van Belle K., Brosens E., Desmyter A., De Gieter M., Wieruszeski J-M., Willem R., Wyns L., Zegers I., Proc. Natl. Accad. Sci U. S. A. 2002, 99, 531.

2. Messens, J., Martins, J. C., Brosens, E., Van Belle, K., Jacobs, D. M., Willem, R., Wyns, L., J. Biol. Inorg. Chem. 2002, 7, 146.

3. Messens, J., Martins, J. C., Van Belle, K., Brosens, E., Desmyter, A., De Gieter, M., Wieruszeski, J-M., Willem, R., Wyns, L., Zegers, I., Proc. Natl. Acad. Sci USA 2002, 99, 8506.

4. Jeffrey, G. A., An Introduction to Hydrogen Bonding, Oxford University Press, New York, 1997.

5. Roos, G., Messens, J., Loverix, S., Wyns, L., Geerlings, P., submitted for publication in J. Phys. Chem. B.

6. a) Smallwood, J. C., McAllister, M. A., J. Am. Chem. Soc. 1997, 119, 11277.
b) Pan, Y., McAllister, M. A., J. Am. Chem. Soc. 1997, 119, 7561. c) Koch, C. W., Holthausen, M. C., A Chemist‘s Guide to Density Functional Theory, Second Edition, d) Wiley VCH, Weinheim, Germany, 2001. e) Mignon, P., Steyaert, J., Loris, R., Geerlings, P., Loverix, S., J. Biol. Chem. 2002, 277, 36770.

Study of geometric properties of phenylene systems through different ab initio methods

M. A. Santos, L. Y. A. Davila, H. M. Petrilli, M. J. Caldas
Institute of Physics, University of Sao Paulo, Brazil
R. B. Capaz
Institute of Physics, Federal University of Rio de Janeiro, Brazil

There is very strong interest in describing accurately the structure of open systems, dependent on interaction between non-bonded atoms, within the Density Functional Theory (DFT) framework. However, for these systems there are crucial regions with very low electronic density, where errors are amplified. A prototypical case found among conjugated polymers is polyparaphenylene (PPP) which consists of a sequence of phenylene rings connected to one another by carbon-carbon bonds in para-position. The torsion angle between rings (a structural parameter that can strongly influence the electronic properties) is affected by the balance between the coulombic repulsion between the hydrogen atoms from neighbour rings, van der Waals attraction and pi-delocalization energies coming from the backbone pi-electrons.
Here we compare DFT methods, within both the Local-Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) to calculate the torsion angle between rings of finite and infinite systems of paraphenylene: molecular biphenyl, crystalline biphenyl and 1D PPP. We have chosen three different basis set expansion models: localized wave functions (SIESTA[1]), plane waves (ABINIT[2]) and mixed-basis set (PAW[3]). We found that the results strongly depend on the XC potential used and that the convergence tests for these open systems must be very stringent.

1. J. M. Soler, et. al. J. Phys.: Condens. Matter 14 (2002) 2745.
2. http://www.abinit.org.
3. P. E. Blochl. Phys. Rev. B. 50 (1994) 17953.

Hydrogen bond interactions and vibrational properties of the hydroxyl groups in dioctahedral 2:1 phyllosilicates by DFT methods

C. Ignacio Sainz-Díaz, Elizabeth Escamilla-Roa and Alfonso Hernández-Laguna

Quantum-mechanical calculations based on linear scaling Density Functional Theory (DFT) approximation with numerical atomic orbitals as basis set and pseudopotentials were performed on dioctahedral 2:1 phyllosilicates samples. Spectroscopic methods are a very useful experimental tool for studying cation distributions in octahedral sheet of these minerals, especially the IR frequencies of OH groups. The calculated ν(OH) and δ(OH) frequencies are consistent with the experimental values for most of the samples with different compositions. Besides, our theoretical study of the cation pair substitution effect on the OH vibration frequencies matches the experimental phenomena. By means of these calculations it is possible to predict the frequency assignment of the out-of-plane deformation vibration of M-O-H bond angle (γ(OH), 500-700 cm^{-1}) of these minerals that is not possible to assign easily experimentally. The study of the OH spatial disposition, the hydrogen bonds and electrostatic interactions of the H atoms is also presented. The effect of the cation substitution on these interactions is interesting to understand experimental behavior of these groups. The vibrations of the OH groups depend significantly on the nature of cations which are joined with, and also on the interactions of the H atom with the tetrahedral O atoms that are surrounding the OH group.

The basis set superposition error effects on the Hartree-Fock and Kohn-Sham orbitals for systems linked by hydrogen bonds

Jorge Garza, Zeferino Ramrez and Rubicelia Vargas
Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana- Iztapalapa. A. P. 55-534, México Distrito Federal México.

The hydrogen bond presented in the systems H_2O-H_2O, H_2O-HF and H_2O-FCH_3, was studied by using the Hartree-Fock, BLYP, B3LYP and MP2 methods. In order to get a systematic study, the basis sets family cc-pVXZ (with X=D,T and Q) was used. The basis set superposition error (BSSE) obtained by each method is discussed in terms of the impact of it on the Hartree-Fock and Kohn-Sham orbitals. With this analysis it is clear why the MP2 method gives the biggest BSSE for any systems linked by hydrogen bonds.

Computational studies of small molecules in condensed phases

Jonathan R Yates, Chris J. Pickard, Francesco Mauri
Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, UK
Francesco Mauri
Laboratoire de Mineralogie-Cristallographie de Paris, Universite Pierre et Marie Curie - Campus Boucicaut, Paris, France

Solid State Nuclear Magnetic Resonance is a valuable probe of hydrogen bonding interactions. Recent developments in experimental techniques have lead to high resolution Oxygen-17 and Hydrogen-1 NMR Spectra for molecular crystals.

First principles calculation of NMR parameters has proven to be an important tool to compliment Solid State NMR spectroscopy. We use a recently developed method, based on density

functional theory and the planewave pseudopotential approach, which allows the calculation of NMR parameters in extended periodic systems.

In recent work on crystalline glutamic acid we used first principles calculations to unambiguously assign the experimental Oxygen-17 NMR spectra and also to find correlations between Oxygen-17 NMR parameters and the strength of hydrogen bonding. Such calculations also provide an important link between experimental observables and the level of theory used.

We present studies of a range of hydrogen bonded molecular crystals including amino acids, sugars and pharmaceutical polymorphs.

A many body study of the cooperative effects in hexamer water clusters

Rafael Almeida
Universida de los Andes, Venezuela

List of participants

Almeida R	Universidad de Los Andes, Venezuela	mata@ula.ve
Angyan J	CNRS-Universite Henri Poincare, Nancy France	angyan@lcm3b.uhp-nancy.fr
Aviyente V	Bocazici University, Bebek, Instanbul	aviye@boun.edu.tr
Baerends EJ	Vrije Universiteit, Amsterdam, The Netherlands	baerends@chem.vu.nl
Benco M	Vienna University, Vienna Austria	lubomir.benco@univie.ac.at
Blum V.	Fritz-Haber-Institut, Berlin Germany	volker_blum@web.de
Castella-Venture M	LADIR/CNRS, Thiais, France	martine.ventura@glvt-cnrs.fr
Dixon DA	University of Alabama Tuscaloosa, USA	dadixon@bama.ua.edu
Elstner M	Universitaet Paderborn, Paderborn Germany	elstner@phys.upb.de
Fuchs M	Fritz-Haber-Institut, Berlin Germany	fuchs@fhi-berlin.mpg.de
Galli G	Lawrence Livermore National Laboratory, USA	galli@llnl.gov
Goursot A.	LMCCCO UMR-CNRS, Montpellier France	goursot@rhodium.enscm.fr
Gruning M.	Donostia International Physics Center, San Sebastian Spain	m.grunning@sc.ehu.es

Grzegorzewski F	Fritz-Haber-Institut, Berlin Germany	franzis@fhi-berlin.mpg.de
Guo H	University of Tennessee, Knoxville USA	hguol@utk.edu
Hakala M	University of Helsinky, Finland	mikko.o.hakala@helsinki.fi
Heady LC	Cavendish Laboratory, Cambridge UK	lch31@cam.ac.uk
Hernandez-Laguna A.	CSIC, Granada Spain	alfonso@eez.csic.es
Hobza P	Academy od Sciences of the Czech Republic, Prage,Czech Republic	pavel.hobza@uochb.cas.cz
Ireta J	Fritz-Haber-Institut, Berlin Germany	ireta@fhi-berlin.mpg.de
Ismer L	Fritz-Haber-Institut, Berlin Germany	ismer@fhi-berlin.mpg.de
Jalkanen KJ	Technical University of Denmark, Lyngby, Denmark	jalkanen@fysik.dtu.dk
Joice S	Cavendish Laboratory, Cambridge UK	sajza@cam.ac.uk
Klein M	University of Pennsylvania, Philadelphia, USA	klein@lrsm.upenn.edu
Kohn W	University of California, Santa Barbara, USA	kohn@physics.ucsb.edu
Laasonen K	University of Oulu, Oulu, Finland	kari.laasonen@oulu.fi
Lozano-Casal P.	University of Edinburgh, Edinburgh, UK	P.lozano-Casal@ed.ac.uk
Marx D	Ruhr-Universitaet Bochum Germany	dominik.marx@theochem.rub.de
Müller-Dethlefs K	University of York, York, UK	kmd6@york.ac.uk
Pollet R	Ruhr-Universitaet,Bochum Germany	rodolphe.pollet@theochem.rub.de
Raugei S	SISSA, Trieste, Italy	raugei@sissa.it
Roos G	Vrije Universiteit, Brussel, Belgium	groos@rub.ac.be
Sainz-Diaz I	CSIC, Granada Spain	sainz@eez.csic.es
Salahub DR	University of Calgary, Calgary, Canada	dennis.salahub@ucalgary.ca
Santos M.	University of Sao Paulo, Brazil	masantos@macbeth.if.usp.br
Savin A	CNRS et Universite Paris VI, Paris, France	savin@lct.jussieu.fr
Sauer J	Humboldt-Universitaet, Berlin, Germany	js@chemie.hu-berlin.de
Scheffler M	Fritz-Haber-Institut, Berlin Germany	scheffler@fhi-berlin.mpg.de
Senet P	Universite de Bourgogne, Dijon, France	psenet@u-bourgogne.fr
Scuseria G	Rice University, Houston, USA	guscus@rice.edu
VandeVondele J.	University of Cambridge, Cambridge, UK	jv244@cam.ac.uk
Vargas-Fosada R.	UAM-Iztapalapa, DF, Mexico	ruvf@xanum.uam.mx
Walker M	University of Edinburgh, Edinburgh, UK	s9813724@sms.ed.ac.uk
Yang W	Duke University, Durham, USA	weitao.yang@duke.edu
Yates J	Cavendish Laboratory, Cambridge, UK	jryz0@cam.ac.uk

4.1.2 Report on the workshop 'First-Principles Simulations: Perspectives and Challenges in Mineral Sciences'

27th September - 1st October 2004 at CECAM, Lyon, France

Organisers

Michele C. Warren, The University of Manchester

Artem R. Oganov, ETH Zurich

Bjoern Winkler, University of Frankfurt

Proceedings of this workshop will be published as part of the series 'Berichte aus Arbeitskreisen der DGK' (http://opal.kristall.uni-frankfurt.de/DGK/berichte/)

Topics

The main topics of the workshop were

1. Latest developments and prospects of theory and methodology from physics and chemistry perspectives(advanced electronic structure methods, metadynamics, excited states, ab initio thermodynamics)
2. Recent advances in the application of these methods to the minerals sciences, with particular attention to extreme conditions in planetary interiors and to processes at mineral surfaces
3. materials whose electronic and/or crystallographic structure pose significant problems to theory (e.g. strongly correlated systems, incommensurate phases, quasicrystals, and non-collinear magnets).

Volker Heine discusses many of these in his concluding remarks, section .

Participants

Donat Adams, ETH Zurich

Maria Alfredsson, University College London

Emilio Artacho, University of Cambridge

Etienne Balan, Université Pierre et Marie Curie

Dirk Bosbach, Forschungszentrum Karlsruhe

Razvan Caracas, Carnegie Institution of Washington

Franz Gaehler, Universität Stuttgart

Mike Gillan, University College London

Xavier Gonze, Université Catholique de Louvain

Volker Heine, University of Cambridge

Sandro Jahn, GeoForschungsZentrum Potsdam

Daniel Jung, ETH Zurich

Juerg Hutter, University of Zurich

Alessandro Laio, ETH Zurich

Caetano Miranda, ICTP, Trieste

Artem Oganov, ETH Zurich

Steve Parker, University of Bath

Chris Pickard, University of Cambridge

Andrew Rappe, University of Pennsylvania

Keith Refson, Rutherford Appleton Lab

Leonid Sandratskii, Max-Planck-Institut fur Mikrostruckturphysik, Saale

Phillipe Sautet, ENS Lyon

Sandro Scandolo, ICTP, Trieste

Viktor Struzhkin, Carnegie Institute of Washington

Joost VandeVondele, University of Cambridge

Viktor Vinograd, Universität Frankfurt

Michele Warren, University of Manchester

Bjoern Winkler, Universität Frankfurt

Quan Yin, New Jersey Institue of Technology

Programme

Monday 27th Sept: Welcome, Surfaces and the Environment		
09:30	*Arrival and coffee*	
10:00	B. Winkler	DFT studies of mineral and related phases.
11:00	*coffee*	
11:30	K. Refson	Surface processes in minerals: computational studies
12:30	*lunch*	
14:00	S. Parker	Atomistic simulation of the structure and stability of mineral interfaces
14:30	M. Warren	Computational environmental mineralogy
15:30	*coffee*	
16:00	D. Bosbach	Processs at mineral / aqueous solution interfaces: experimental studies on clay minerals and calcite
17:00	*end*	
Tuesday 28th Sept: Pressure, temperature and phase diagrams		
9:00.	S. Scandolo	Computational studies of planet-forming materials
10:00	M. Gillan	Ab initio thermodynamics
11:00	*coffee*	
11:30	A. Oganov	Phase diagrams of minerals from first principles
12:30	*lunch*	
14:00	M. Alfredsson	Hybrid DFT calculations on phase transitions in FeO
14:45	C. Rodrigues-Miranda	Computational rheology of MgO at mantle pressures
15:30	*coffee*	
16:00	D. Jung	Decomposition of CaSiO3 perovskite: an ab initio study
16:30	D. Adams	Molecular dynamics simulations of cubic CaSiO3 at lower mantle conditions
17:00	*end*	
Wednesday 29th Sept: dynamics and spectroscopy		
09:00	J. VandeVondele	Ab initio molecular dynamics in CP2K/Quickstep
10:00	A. Laio	Metadynamics
11:00	*coffee*	
11:30	X. Gonze	Density-functional perturbation theory, and its applications in mineral sciences
12:30	*lunch*	

14:00	E. Balan	First principles calculation of the infrared spectrum of phyllosilicates : the special case of chrysotile nanotubes
15:00	P. Sautet	Interaction of water with microporous aluminophosphates.
16:00	*Time to explore Lyon!*	
Thursday 30th Sept: advanced electronic structure		
09:00	C. Pickard	The first principles prediction of the magnetic resonance parameters of minerals
10:00	A. Rappe	Pseudopotentials for Ab initio modeling of minerals
11:00	*coffee*	
11:30	L. Sandratskii	Non-collinear magnetism: computational studies
12:30	*lunch*	
14:00	J. Hutter	Time-dependent density functional theory applied to molecules in solution
15:00	*coffee*	
15:30	Q. Yin	DMFT study of FeS
16:00	V. Vinograd	Thermodynamics of mixing and ordering in silicates and oxides from static lattice energy and ab initio calculations
17:00	*end*	
Friday 1st Oct: aperiodic systems and methods for large systems		
09:00	R. Caracas	Ab initio simulations of incommensurate phases
10:00	F. Gaehler	Computational studies of quasicrystals
11:00	*coffee*	
11:30	E. Artacho	Network equilibration and first principles liquid water
12:30	*lunch*	
14:00	S. Jahn	Generation of transferable interatomic potentials for oxide materials from ab initio DFT calculations
15:00	*coffee*	
15:30	V. Heine	Summary and points for discussion
16:15	Round table discussion	
17:00	*end*	

Concluding Remarks by Volker Heine

Volker Heine, Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE

This workshop has set a new milestone in Computational Mineralogy, and I am sure you will join me in thanking the organisers, the financial sponsors and all who have given talks and contributed to the discussion, i.e. all of us.

The workshop sets a new milestone. One speaker quoted TS Duffy writing in Nature 'News and Views' that "A new era of mantle research has begun." But not only in mantle research: we have seen that computer simulation is solving real problems in all sorts of directions. Computation has truly joined the mainstream in mineralogy and crystallography. I think that is the main message from this workshop.

We can see the breadth of the applications by noting the types of material mentioned: minerals of all kinds including the structure of the D" layer at the bottom of the mantle, the liquid and solid iron core, Al/Si ordering, thermodynamics of garnet solid solutions, zeolite-like structures of $AlPO_4$, chrysolite tubes, incommensurate phases and quasicrystals, magnetic materials with non-collinear atomic moments, and more. Applications include phase diagrams, surfaces and interfaces, and there has been a lot of discussion of simulating water accurately with a view to the study of wet surfaces of environmental interest. An important role of simulation is to help interpret data such as infrared and NMR spectra, and the suggestion has been made that theory and codes are needed for a greater range of probes. The programme also contained talks on a substantial range of advances in simulation techniques such as linear scaling, better pseudopotentials, better classical models of interatomic forces, the Quickstep code, TD-DFT, DMFT, and more. I will talk specifically about free energy calculation in a moment.

Computer simulation joining the mainstream in mineralogy raises the question 'What should be an ideal ratio of computationalists to experimentalists in an active research institute?' It will depend on the particular area of research, but I would suggest in many cases a ratio of about one to three. Anyway the issue may need to be brought to the attention of decision makers in appointments etc., often older men who may not be fully in touch. Another implication is to publicise it to pupils in secondary schools who are considering what undergraduate degree subject to choose. So far the computationalists in mineralogy have been recruited largely from physics and chemistry, which is healthy because they also bring some new perspectives, but computational mineralogy has matured sufficiently that it must recruit more from within the earth sciences community itself.

Another aspect of computer simulation going mainstream in mineralogy is that people need to have an integrated research programme in which 'computer experiments' and laboratory experiments are planned together as complementary tools from the beginning in the same way as different types of experiment are. Some examples of that have been evident at this workshop, but there are only a few groups having routinely such an approach. In the field of surface chemistry Professor David King (in Cambridge) is such a person: I remember him showing a photo of his research group and saying "The people on the left side are the computationalists and without them there would be whole areas of research which we would not be able to touch".

The pressure to move into areas of environmental relevance has been mentioned. Of course similar pressures in research are nothing new, and are to a considerable extent justified if done intelligently. It is dishonest to ignore that the taxpayer puts a lot of money into science compared to research in the humanities because of the technological and economic factor. Moreover being a pioneer in a relatively new research field is fun, as many of us here can testify. While a positive nudge via extra research funding is one thing, a bludgeoning sledgehammer is wholly destructive.

I want to mention particularly one, or rather two, impressive technical advances that will forever mark out this workshop for me. At the first workshop in 1997 and even the second one in 2001, practically all simulations corresponded to zero Kelvin. Now not only has finite temperature become routine where relevant, but also the actual calculation of free energies and other thermodynamic variables. For example Gillan showed no less than three separate methods of establishing the P/T melting curve for iron under conditions in the earth's core, and insisted that that they must be refined until they all three agree. Also one now calculates the composition and structure of an oxide surface thermodynamically as a function of the partial pressure of oxygen in the atmosphere above the surface.

In this context of calculating free energies the talk by Laio can only be described as stunning, describing a real breakthrough in Parrinello's group which they call 'metadynamics'. It serves two purposes. Firstly it calculates the free energy around some metastable (or stable) minimum, but more importantly it nudges the system in a controlled way into any other minimum while tracking the free energy along the way, without having to know where that other minimum lies or any idea of the transition pathway. The method promises to make a major contribution in various fields including solid state phase changes. Indeed I will suggest later its application to what I consider an interesting question which we could not really tackle before.

As a physicist working on electronic structure, I am not well versed in waltzing around complex free energy surfaces, and so I have had some initial difficulty in understanding the metadynamics method. A few words here may therefore help other physicists. (A longer illustrated tutorial was given at the workshop.) We start by defining some coordinate Q which describes some characteristic feature of the initial state and which is expected to alter noticeably in any substantial structural change. It might be something like $Q = D(12) - D(34)$ where $D(nm)$ is the distance between atoms n and m. We then do a Car Parrinello (C-P) run of the system oscillating under the Kohn Sham (K-S) Hamiltonian at temperature T around our initial state A, and then plot out the probability distribution $P(Q)$. The crux of the method is that $P(Q)$ gives information about the free energy well $F(Q)$ around that minimum A: the peak of the distribution tells one the position Q_1 of the minimum, and the width of $P(Q)$ indicates how broad or narrow the well is in comparison with kT. One can therefore express $F(Q)$ around the minimum approximately by a Gaussian (or other convenient function)

$$F(Q) \approx (\text{const}) - A_1 \exp[\frac{-(Q - Q_1)^2}{B_1}]. \tag{1}$$

Note that $P(Q)$ is determined by the free energy. The $P(Q)$ is not just proportional to the Boltzmann exponential of the energy but contains also the prefactor $W(Q)$ from the amount of phase space occupied by the other $(3N - 1)$ variables where N is the number of atoms. The W is of course related to the entropy $S = k \log W$, and so combining $W(Q)$ with $\exp[E/kT]$ we obtain

$$P(Q) \propto \exp[\frac{-F(Q)}{kT}]. \tag{2}$$

The novel trick is now to run a second C-P simulation for a new modified system defined by the Hamiltonian

$$\begin{aligned} H &= V_1(Q) + H(K-S) \\ &= +A_1 \exp[\frac{-(Q-Q_1)^2}{B_1}] + H(K-S) \end{aligned} \tag{3}$$

where the first term is called the metapotential $V_1(Q)$. Since Q is a known function of the atomic coordinates, one can calculate the additional forces on the atoms due to the first term in (3). Note the plus sign in the metapotential in (3), contrary to the minus sign in (1). The metapotential has therefore partially 'cancelled' or 'filled in' the well of $F(Q)$ around the minimum A, so that the new C-P run gives a new distribution $P_1(Q)$ considerably broader than before. This $P_1(Q)$ defines a new Gaussian free energy

$$(\text{const}) - A_2 \exp[\frac{(Q-Q_2)^2}{B_2}] = (\text{const}) - V_2(Q) \tag{4}$$

to describe the $F(Q) + V(Q_1)$. One then uses this new metapotential $V_2(Q)$ to 'fill in' or 'cancel' some more of the A-well in $F(Q)$ in a new C-P run with Hamiltonian

$$H = V_1(Q) + V_2(Q) + H(K-S), \tag{5}$$

and one continues this process until the whole of the well in $F(Q)$ around A has been filled in. One notices that by the system making a transition to a new well B around some new Q_B. So one has mapped out the whole of the free energy

$$F(Q) = \sum_i A_i exp[\frac{(Q-Q_i)^2}{B_i}] \tag{6}$$

around the minimum A, and one can continue to map out $F(Q)$ around the new minimum B if one wishes. At any rate one has discovered computationally the path and free energy barrier from A to B. I hope this description is helpful. Note that any error in $V_1(Q)$ will tend to be picked up and compensated in $V_2(Q)$, but the amplitudes of the steps A_i should not be too large because the whole process seems to me in some sense analogous to thermodynamic integration with the $V_i(Q)$ being the isothermal work done in building up (6). There is a formula which gives the accuracy of $F(Q)$ in terms of the amplitudes A_i and the duration times of the C-P runs so that one can optimise the whole procedure.

Several speakers at the workshop described using ab initio calculations to parameterise a semi-classical potential model which was then applied to much larger simulations, i.e. larger in dimension or longer in run time. This is a very important methodology and some excellent work was reported at this workshop, validated with the greatest of care. I specifically mention the validation because unfortunately the subject is littered with disappointments: one cannot force nature into the preconceived mold of some potential model if that does not do justice to reality. Bonding, dispersion forces, polarisability and deformability of atoms or ions are all quantum phenomena, and there is no guarantee that a classical model will represent the results well. Let me mention the history of Jerry Tersoff working over about ten years to develop a classical bonding model for silicon. This should be a prime candidate for a classical model: one type of atom only, nice covalent bonds, without the ambivalence of carbon between tetrahedral and graphite-like coordination. Tersoff fitted as many experimental data and good DFT calculations as were available, including defects, surfaces and surface reconstruction, clusters etc., using both structures and energies. Then each year he would honestly test the model on new data or calculations that had become available, and would adjust the model accordingly. So there is a whole history of models Tersoff I, Tersoff II, and so on, going up to some number of order a dozen. The point is that each time the previous model did a very disappointing job of fitting the new data. A few years later I was at a conference where some DFT calculations were shown of the energy barrier for vacancy diffusion which turns out to be a slightly complicated process involving the rotation of a pair of atoms. Anyway the DFT calculations were compared with the best three Tersoff models and there was no agreement at all, neither between the different Tersoff models nor with the DFT results: the discrepancies were of the order of 100 percent. The last time I met Tersoff was at a DFT conference (!) and he agreed that the complexity of silicon bonding could not be described by a classical model where there are serious changes in bonding such as in defects and at surfaces, let alone small clusters. But of course a model may exist for some limited range of configurations, e.g. phonons as the simplest example. One might reasonably hope that ionic materials are easier, but I think that any honest use of language would have alumina for instance having at least some degree of covalent bonding which might be altered in a complicated way at a defect or surface that is not contained in a 'ionic' model. Certainly the electron density in 3s and 3p orbitals is not zero near the centre of the aluminium ion. I notice that the ionic models described at this workshop did not seem to include fitting to surface, defect or cluster calculations.

A story that I told at the dinner on Wednesday evening showed that there can be substantial cultural differences in what one understands by the word 'understanding'. I give two instances here. Charles Geiger once said "From my perspective as an Associate Editor, I can see that mineralogy has come to the end of the road as a purely descriptive science. It has to become more quantitative and to ask the question 'why?'." That relates to the older culture which seemed to equate understanding with determining the crystal structure. A mistaken newer culture is illustrated by the story of when I visited John C. Slater's group at MIT in 1956. I had developed my own ideas rather in isolation as a PhD student in Cambridge about how to treat self-consistency, exchange and correlation in an electronic band structure calculation, and I asked Slater what his group thought about these questions, to which he replied "They seem to prefer calculating rather than thinking." These two issues about our purpose also surfaced occasionally during the present workshop. I think that as scientists we wish to understand the world, not just accumulate data about it. A good example is the sequencing of the whole of the human genome, a stupendous achievement: but all that information is as yet totally useless until we learn what the different bits are for. I am quite clear what I mean by 'understanding' as a theoretical or computational physicist. Firstly I want to see identified what are the dominant factors in a situation, encapsulated in a simplified story or 'back of the envelope' mathematical model that explains convincingly the qualitative features of the phenomenon. Here the simpler the model, the more pared down to the bones, the more revealing it is. Secondly I want to see the explanation tied to the basic laws of physics, not just to arbitrary notions. Thirdly I like to have a full calculation or simulation that takes all the factors into account as far as one can, to confirm that the simplified model is indeed valid. I have to admit that I have often not achieved the third part. On the one hand it is rather boring and could well take several years of work, and on the other hand the model may be sufficiently convincing when taking into account corroborating evidence from all else one knows of the field. Life is short! But as an example of all three parts, there is some work we did on quartz which I mentioned during the discussion of incommensurate phases. In going down in temperature from the beta to the alpha phase, there is a stable intermediate incommensurate phase over a narrow temperature range. A simple structural diagram of the structure explains the direction that the incommensurate modulation because it only involves rotation of the tetrahedra without distorting them. Symmetry theory then shows that in this direction the soft mode interacts with one of the acoustic modes away from $k = 0$ but not at $k = 0$. That means the interaction increases with k from zero, and a simple 2×2 secular equation for the two modes shows how one of them as a mixed mode is driven to instability before the soft mode frequency at $k = 0$ has itself hit zero. This is what I call the 'story' and with a bit more detail the 'model'. In this case we did look at the full phonon calculation to pick out the forms and the magnitudes of the relevant matrix elements of the dynamical matrix.

The question of discovering new phases was raised, with mention of examples where a new phase was first noticed computationally, particularly at high pressure. There does not seem to be any unique or foolproof way of discovering new phases beyond using 'trial and error' with chemical intuition , although systematic approaches have been suggested. There seems to be little such 'trial and error' searching, and I wonder whether more might be rewarding. I would like to mention here the historical work of Berndt Matthias who was a chemist at Bell Labs, trying to reach the highest superconducting transition temperature, at that time a bit above 20 Kelvin before the discovery of the cuprate superconductors. In his lab you could see hundreds of compounds he had made, but it was not just mindless mixing. With experience he found two principles that helped guide him in what to try. One was that compounds containing niobium seemed to be good, and another was that complex crystal structures such as the A15 structure also helped to lift the superconducting transition temperature, both of which rules we can now understand theoretically. So my question is "Who will be the 'Berndt Matthias' of computational mineralogy?" To try a compound in the computer is probably faster than making it and determining the structure in the laboratory, so why not try? The new metadynamics has been suggested as a search tool.

I turn now to a favourite theme of mine, namely 'quick and dirty' ab initio calculations. It is not a popular subject. As one young friend explained to me, a reputation for 'quick and dirty' is not the route to a professorship in theoretical physics in his country! But if one can get a speed up of a factor of 100 compared with a usual plane wave code, then one has the chance to do wholly new science. By 'quick and dirty' I mean something like Density Functional Theory projected onto a simplified tight binding model with a minimal basis set or near it. Incidentally there is always a potential entering such a model and one can use the variational principle to make the calculation variational with respect to that potential as well as to the wave function. I think such a model would do a better job of describing significant rebonding than a classical model: see comments above. Ten years ago Jose Ortega had that factor of 100 in speed with Otto Sankey's code, and used it to try to see how Si/Al interchange actually occurred in Si/Al ordering in tetrahedral framework silicates. Limited Castep calculations of pulling the Si and Al atoms out of their tetrahedra had not made much sense, and so we did a dynamic run after giving the system a helluva heat pulse just to get some action and some insight from seeing what happened. Unfortunately the research came to a premature end when Ortega was recalled to a tenure track position and killing teaching load in Madrid. Someone asked whether quick and dirty calculations are of any use if one doesn't know how dirty they are. In fact we monitored the energy by doing an occasional Castep calculation in the dynamic run, and found an approximately constant conversion factor. If the factor is truly constant within the system we had, then it would imply that the course of the dynamics was correct except for the absolute speed which would be subject to the same adjustment factor. In any case I deprecate such a negative question. Firstly the situation is no different with fitted classical potentials where one does not know the errors outside the fitted database, as already discussed. Secondly the situation is no different in some laboratory experiments, where I have heard heated arguments about what temperature was reached by laser heating in a diamond anvil cell. Thirdly exploratory calculations are what they say they are, namely exploratory. Fourthly with a speed factor of 100 in hand, one can afford proper calculations every now and again to test and monitor what one finds, as we did. Fifthly such quick and dirty calculations might be of use as the initial model for a thermodynamic integration. However the new technique of metadynamics may make such a quick and dirty approach obsolete in some cases. For example I suggest the problem of how Si/Al exchange takes place as a prime example for a metadynamics calculation.

On that positive note, I look forward to a 2007 workshop which may appropriately be called "Ten Years After" (after the first workshop in 1997), which I am sure will feature many exciting advances.

4.1.3 Report on ESPA-2004 Workshop

ELECTRONIC STRUCTURE: PRINCIPLES AND APPLICATIONS

UNIVERSITY OF VALLADOLID, SPAIN

September 15-17, 2004

ORGANIZING COMMITTEE:

Antonio Largo, Inmaculada García, Carmen Lavin, Carmen Barrientos, Pilar Redondo,
Universidad de Valladolid, Departamento de Química Física, Spain.

Luis C. Balbás, *Universidad de Valladolid, Departamento de Física Atómica, Spain.*

General

The scope of this workshop was to consolidate an existent forum of Spanish theorist on computational chemical-physics in a more international context by increasing the participation of scientist from other countries. Aside from this general purpose, the present edition of the conference dedicated special attention to the methods and theoretical applications dealing with chemical reactivity studies, as well as to recent advances in DFT, its applications in chemistry and how comparison with experiments behaves. Additionally, other techniques applied in the study of the molecular structure, heterogeneous catalysis, biomolecules, chemistry of transition metal systems, etc...has been addressed.

The program consisted of 21 invited lectures and two poster sessions with 69 and 70 posters respectively. The combined number of participants of the meeting was 180 from sixteen different countries (including 53 female and 21 invited speakers).

Descripcion of conferences and disscussions

The invited talks covered

I) Fundamental topics

II) Applications to: Perovskites, Mass spectrometry, Organometallics, Mechanical embedding, semiempirical methods, Enzymatic catalysis, Weak interactions, Reactions, Other topics.

Joan Bertran in the Summary Report: The separation between methodology and applications, as long as the objective of a science is to solve real problems, is bridged by the increase in computational power. Chemistry is no more exclusively an experimental science.

Fundamentals and methodology:

Methodology developments have a triple objective: Bigger, Accurate, Faster. Van Vleek catastrophe: "In general the many electron wave-function for a system of N electrons is not a legitimate scientific concept, when $N \geq 10^3$".

Sánchez de Mers: New algorithm based on the Cholesky decomposition of two-electron integrals.

Bartlett, Becke, Scuseria, and Soler: Improvements on DFT exchange correlation functional to solve problems with some radicals, reaction energy barriers, charge transfer complexes, Rydberg excited states and van der Waals interactions. Some problems arise from the self-interaction error. New ideas about an Exc functional with dependence on the density of states (Soler).

Solid state applications:

The solid state is the traditional field of DFT.

Borstel: point defects in perovskite crystals. F-type centers. O vacancies with trapped electrons. Hole polaron bound cation vacancies. Large-scale computer modeling combining quite different approaches, ranging from first principles (FP-LMTO) to semi-empirical (INDO) and classical (shell model) methods.

Kotomin: ABO3 perovskite surfaces within CRYSTAL code and different Exc functionals lead to surprisingly good agreement with classical shell model calculations. Surface rumpling and relaxation compared with relevant experimental data. Preliminary results for the oxygen adsorption and diffusion on perovskite surfaces.

Mass spectrometry:

Otilia Mo: gas phase ion-molecule interactions. Dative bonds are favored by the polarization of the molecule and by the electron affinity of the ion.

Ugalde has presented a related topic: the stability of anions in a plasma environment modeled by a statistically screening potential of the Yukawa-type (exp(-lr)/r). Different behavior of systems with a positive and negative electro-affinity and between ground and excited states.

Organometallic:

Einsenstein has shown how the nature of ligands, substituents and counter-ions can determine the structure and behavior of transition metal complexes. B3LYP method and QM/MM for the larger systems.

Revival of semiempirical methods:

Manolo Ruiz: substitution of gaussian correction functions (GCF) in the core-core repulsion terms by a parameterized interaction function (PIF).

Persico: has presented direct semi-classical simulations of photochemical processes with semiempirica wavefunctions. He has developed a semiempirical CI method. This allows studying photochemical processes in solution by means of QM/MM.

Aschi: has included electrons in complex molecular systems by means of perturbed matrix methods. The philosophy of this method is the inclusion of the electrons in a fast space sampling. The perturbation may be an uniform or non-uniform electric field.

Enzymatic catalysis:

Cramer: dioxygen activation at monocopper enzyme models. Cu/O2 adducts coordinated to biomimetic ligands. The focus of attention has gone from the chemical system to the protein.

Moliner: towards a rational design of catalytic antibodies.

Weak interactions:

Sordo: has studied weakly-bound systems. The effect of charge transfer is important but other terms must be considered.

Hobza: hydrogen-bonds and stacking in DNA. Dispersion forces are well calculated with MP2, since there is a compensation between CBS (complete basis set) stabilization and CCSD(T) de-stabilization energies respect to MP2 results.

Reactions:

Clary: has presented a quantum-dynamical treatment of reactions in small systems from a reduced surface build on a few points calculated at high level. He has also presented the prediction of structures of biomolecules showing the importance of taking into account anharmonicity and quantum effects.

Other topics:

Pyykkö: new predicted heavy-element species. Some of these predictions have been confirmed experimentally $[Au{=}C{=}Au]^{2+}$. Analogy between platinum and oxygen (CPt2)

Solá: Aromaticity from delocalization indices. First and second (ρ, $\nabla^2\rho$), generation of Bader's indices, ELF (electron localization function) and DI (delocalization index), which is the number of electrons delocalized or shared between atoms A and B.

Posters:

136 posters in two sessions covering different topics:

- CASSCF, CASPT2, MRCI, FCI.
- Chemical reactions (potential surfaces; mechanisms; variational transition state; dynamic studies; reactions in solution). Photochemistry.
- Adsorption in surfaces. Nanotubes. Solid state.
- Clusters, protein-ligand interactions, organometallics.

Abstracts of invited talks

AB INITIO DFT: PROBLEMS AND PROSPECTS

Rodney J. Bartlett, Victor Lotrich, Igor Schweigert

Quantum Theory Project, PO Box 118435, University of Florida Gainesville, FL, USA
32611-8435

In our efforts to tie wavefunction theory and density functional theory together in a seamless fashion, we have introduced ab initio dft as an approach that has the following properties of ab initio methods: (1) Guaranteed convergence to the right answer in the basis set limit; (2) Use of orbital dependent functional for the correlation energy taken from wavefunction (MBPT/CC) theory; (3) Solution in a gaussian basis set with no need for numerical quadrature. In this way, we obtain purely local, orbital dependent, exchange-correlation potentials. This talk will report on our experience in determining such potentials and applying them to weak interactions, potential energy surfaces, and other properties. In particular, we show that ab initio dft offers a kind of 'best' second-order MBPT approximation that exceeds that of MP2.

REDUCED SCALING IN THEORETICAL CHEMISTRY USING CHOLESKY DECOMPOSITION

Alfredo M.J. Sánchez de Merás[a], Henrik Koch[b], Thomas B. Pedersen[c]

[a]Dpt. Physical Chemistry. ICMol, University of Valencia (Spain)
[b]Dpt. Chemistry, Trondheim University (Norway)
[c]Dpt. Theoretical Chemistry, University of Lund (Sweden)

In this communication we present a novel algorithm based on the Cholesky decomposition of two-electron integrals. In this way important savings are obtained both in the number of integrals to calculate and in storage requirements. Using Cholesky-decomposed integrals it is possible to efficiently carry out energy and property calculations with a predefined accuracy. The method will be illustrated with applications focused on interaction-energies, polarizabilities and optical activities.

RECENT PROGRESS IN THE DEVELOPMENT OF EXCHANGE-CORRELATION FUNCTIONALS

Gustavo E. Scuseria

Department of Chemistry, Rice University, Houston, Texas 77005, USA

This presentation will address our current efforts to develop more accurate exchange-correlation functionals for DFT. The functionals to be discussed include a new meta-GGA denoted TPSS [1], a screened exchange hybrid especially designed with solids in mind [2], local hybrids [3], and a current (j) dependent extension of PBE [4]. Extensive benchmarks and applications will also be presented.

[1] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).

[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).

[3] J. Jaramillo, M. Ernzerhof, and G. E. Scuseria, J. Chem. Phys. 118, 1068 (2003).

[4] S. N. Maximoff, M. Ernzerhof, and G. E. Scuseria, J. Chem. Phys. 120, 2105 (2004).

EXCHANGE AND CORRELATION AS A FUNCTIONAL OF THE LOCAL DENSITY OF STATES

José M. Soler

Departamento de Fsica de la Materia Condensada, C-III,

Universidad Autnoma de Madrid, E-28049 Madrid, Spain

Although the classical work of Hohemberg and Kohn showed that the total electronic energy can be expressed as a functional of the electron density alone, the practical implementation of Kohn and Sham already made use of further intermediate information (the free electron orbitals that produce that density) to generate an accurate enough functional. More recently, the so-called meta-GGAs [1,2] make further use of the free electron orbitals, to calculate a kinetic energy density for improving the exchange and correlation (xc) part of the functional Exc. In principle, there is no limit for the number of intermediate variables that can be used to improve the functional, but one needs a physically motivated procedure, preferably nonempirical, to define the functional form. I propose to use the whole local density of occupied states r(r,e) where e is the local kinetic energy, as a functional variable for Exc. Part of the motivation, as well as the practical parameterization procedure, arises from recent works [3,4] that decompose the xc hole in scattering states (geminals) of two electrons, interacting with an effectively screened Culomb repulsion, with different relative kinetic energies and angular momenta. The key idea is that the interaction of two electrons depends on their relative kinetic energy, which in turn depends on the kinetic energy of each electron. This simple concept leads to an unambiguous local approximation [5], completely specified from first principles, for Exc[r(r,e)]. In its practical Kohn-Sham-like form, the free-electron orbitals yi(r) become the independent variables, and an explicit formula for the functional derivative of Exc[yi(r)] is obtained. The resulting potential is orbital dependent, lowering most the eigenvalues in regions with a high density of occupied states, what might improve the description of energy gaps. The exchange and correlation energy is no longer invariant with a localized-to-extended transformation of the occupied states, what might also help in the description of electron localization and magnetism.

References:

[1] A. D. Becke, J. Chem. Phys. (1998) 109, 2002.

[2] J. Tao et al, Phys. Rev. Lett. (2003) 91, 146401.

[3] A. W. Overhauser, Can. J. Phys. (1995) 73, 683.

[4] P. Gori-Giorgi and J. P. Perdew, Phys. Rev. B (2001) 64, 155102.

[5] J. M. Soler, Phys. Rev. B (2004) 69, 195101.

POST-HARTREE-FOCK CORRELATION FUNCTIONALS

Axe D. Becke

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

We have recently proposed correlation models which can be partnered with exact Kohn-Sham or Hartree-Fock exchange (J. Chem. Phys. 119, 2972, 2003). Thus the well known problems associated with local exchange approximations are solved. We will report our latest test results on thermochemical and kinetic (i.e. barrier height) benchmark sets.

LARGE SCALE COMPUTER MODELING OF POINT DEFECTS IN PEROVSKITE CRYSTALS

G. Borstel and R. I. Eglitis

Department of Physics, University of Osnabrck, D-49069 Osnabrck, Germany

We discuss the current status of large-scale computer modeling of point defects in advanced perovskite crystals combining quite different approaches, ranging from first principles (FP-LMTO) to semi-empirical quantum chemical (INDO) and classical (shell model, SM) methods. Results for basic intrinsic defects include F-type electron centers (O vacancy with one or two trapped electrons) and hole polaron bound cation vacancies. Special attention is given to the calculation of absorption energies and defect level positions within the band gap of the crystal, important for optical applications. We demonstrate that a considerable covalency of the perovskite chemical bonding makes the F-type centers therein much more similar to defects in partly-covalent quartz-type oxides rather than the conventional F centers in ionic alkali halides and MgO. Both one-site (atomic) and two-site (molecular) hole polarons are expected to co-exist, characterized by close absorption energies. SM and INDO simulations of the F center diffusion indicate that the relevant activation energy is quite low, approx. 0.8 eV, which is close to the experimental data. Our quantum chemical INDO calculations confirm the existence of self-trapped electron polarons in KNbO3, KTaO3, BaTiO3 and PbTiO3 crystals. The relevant lattice relaxation energies are typically 0.2 eV, whereas the optical absorption energies lie around 0.8 eV. We also used the INDO method for modeling the atomic and electronic structure of KNbxTa1-xO3

(KTN) perovskite solid solutions. The Nb impurities in KTaO3 reveal clear off-center displacements starting at the smallest calculated concentrations. The magnitude of the Nb off-center displacement is close to the EXAFS observation. In contrast, Ta impurities in KNbO3 always remain on-center, due to higher ionicity of Ta compared to Nb. Using the calculated energy gain due to the off-center displacement of Nb atoms for several concentrations of Nb in KTN, we construct the Ginzburg-Landau-type functional for the excess energy. The coefficients of this functional are concentration-dependent. This dependence allows us to define the type of the concentration-induced phase transition in KTaO3 alloyed by Nb.

First principles calculations of the atomic and electronic structure and reactivity of ABO3 perovskite surfaces

E.A. Kotomin[1] and E. Heifets[2]

[1]Max Planck Institut fr Festkrperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

[2]California Institute of Technology, Pasadena CA 91125, USA

In this paper, we give a review of our recent first-principles calculations of the atomic and electronic structure of different ABO3 perovskite surfaces, including neutral (100) and polar (110) surfaces of BaTiO3, SrTiO3, KNbO3 and LaMnO3. These calculations are performed using Hartree-Fock-LCAO method with a posteriori electron correlation corrections, DFT with 6 different exchange-corelation functionals, including HF-DFT B3LYP hybrid method, as implemented into CRYSTAL-98 computer code. We discuss the implementation of the slab model and surface reconstructions necessary for a polar surface stability. The obtained surface energies, relaxation and rumpling are in a surprisingly good agreement with classical shell model calculations. The polar (110) surfaces reveal much stronger deviation from the bulk properties as compared with the (100) surface. We analyze covalency effects near the surface and compare surface rumpling and relaxation with relevant experimental data. We discuss also preliminary results for the oxygen adsorption and diffusion on perovskite surfaces which is the first step in modelling sensors and fuel cells.

AROMATICITY QUANTIFIED FROM THE ATOMS IN MOLECULES DELOCALIZATION INDICES

Miquel Solá, Eduard Matito, Miquel Duran, Xavier Fradera, and Jordi Poater

Institut de Química Computacional and Departament de Química, Universitat de Girona,
17071 Girona, Catalonia, Spain

Aromaticity is a concept of central importance in physical organic chemistry.[1-6] It has been very useful in the rationalization of the structure, stability, and reactivity of many molecules. Even though this concept was introduced 139 years ago,[7] it has no precise and generally well-established definition yet. Aromaticity is not an observable quantity, and so, not being directly measurable, it must be defined by convention. Because of the importance of aromaticity in chemistry, there have been many attempts to rationalize and quantify this property, and to derive a universal quantitative measure of it. However, because of its multiple manifestations, there is not yet any generally accepted single quantitative definition of aromaticity. The evaluation of aromaticity is usually based on the classical aromaticity criteria: structural, magnetic, and energetic-based measures.[5,8] In this work, new local aromaticity measures defined from the Bader's electron delocalization index (DI) are introduced.[9,10] These new electronic criteria of aromaticity are founded on the fact that aromaticity is related to the cyclic delocalized distribution of p electrons. We have found that these new indicators of aromaticity and the harmonic oscillator model of aromaticity (HOMA) index are strongly correlated for a series of rings in several planar and curved polycyclic aromatic hydrocarbons (PAHs). The correlation between these indices and the nucleus independent chemical shift (NICS) values is less remarkable. We discuss the reason of the differences for a series of selected systems such as pyracylene[11] among others.

References

[1] P. v. R. Schleyer, Chem. Rev. 2001, 101, 1115.

[2] P. J. Garrat, Aromaticity, John Wiley and Sons, New York, 1986.

[3] V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, Aromaticity and Antiaromaticity: Electronic and Structural Aspects, John Wiley and Sons, New York, 1994.

[4] P. v. R. Schleyer, H. Jiao, Pure Appl. Chem. 1996, 68, 209.

[5] T. M. Krygowski, M. K. Cyraski, Z. Czarnocki, G. Hfelinger, A. R. Katritzky, Tetrahedron 2000, 56, 1783.

[6] L. T. Scott, J. S. Siegel, Tetrahedron 2002, 57, 9.

[7] A. Kekul, Bull. Soc. Chim. Fr. (Paris) 1865, 3, 98.

[8] A. R. Katritzky, K. Jug, D. C. Oniciu, Chem. Rev. 2001, 101, 1421.

[9] J. Poater, X. Fradera, M. Duran, M. Solá, Chem. Eur. J. 2003, 9, 400.

[10] E. Matito, M. Duran, M. Solá, in preparation.

[11] J. Poater, M. Solá, R. G. Viglione, R. Zanasi, submitted to Chem. Eur. J.

NEW PREDICTED HEAVY-ELEMENT SPECIES

Pekka PYYKKÖ

Department of Chemistry, University of Helsinki, P.O.B. 55, FIN–00014 Helsinki, Finland

Ab initio quantum chemistry and isoelectronic thinking can be used to predict new inorganic species. A recent example [1] are the surprisingly stable Group-4 tetra-azides, $M(N_3)_4$, which are lower-lying isomers to the $(N_5)M(N_7)$; M = Ti, Zr, Hf, Th, predicted earlier. An even wilder proposal are the metal pentazoles [2], having N:M ratios of up to 40:1.

The closed-shell icosahedral WAu_{12} was reported earlier and has now been made. We also confirm the presumed $[Au{=}C{=}Au]^{2+}$ structure of a mass-spectroscopically observed CAu_2^{2+} species and predict the isoelectronic CPt_2 [3]. Both resemble CO_2 and the platinum-oxygen chemical analogy yields numerous new species. In fact platinum is a 'better oxygen than oxygen', yielding a predicted, bound PtXe [4].

The latest news include the triple-bonded triatomic NUIr [5], the 24-carat 'golden fullerene' Au_{32} and comparative studies of Pt and Ds (darmstadtium) chemistry.

[1] Gagliardi, L.; Pyykkö, P., Inorg. Chem. 2003, 42, 3074.

[2] Straka, M.; Pyykkö, P., Inorg. Chem. 2003, 42, 8241.

[3] Pyykkö, P.; Patzschke, M.; Suurpere, J. Chem. Phys. Lett. 2003, 381, 45.

[4] Burda, J. V.; Runeberg, N.; Pyykkö, P. Chem. Phys. Lett. 1998, 288, 635.

[5] Gagliardi, L.; Pyykkö, P., Angew. Chem. 2004, 116, 1599; Int. Ed. 2004, 43, 1573.

WHY STUDY WEAKLY-BOUND SYSTEMS?

Jos A. Sordo

Laboratorio de Química Computacional, Departamento de Química Física y Analítica,
Facultad de Química, Universidad de Oviedo, C/Julián Clavería 8, 33006, Oviedo, Spain.
e-mail: jasg@uniovi.es

Spectacular advances in high-resolution spectroscopic techniques using supersonic expansions as well as the also impressive parallel developments of computer technology and electronic structure theory favored the study of weakly-bound complexes (1). The analysis of the nature of the forces involved in the formation of such complexes (2,3) is of fundamental importance to gaining a deeper understanding of bulk materials, a subject of value not only in chemistry and physics, but also in biology. On the other hand, the presence of weakly-bound systems on the potential energy surfaces of chemical reactions allows for the interpretation of a number of structural, thermodynamic and kinetic aspects of the mechanisms through which such processes proceed (4).

(1) Chem. Rev. 88, (1988); 94, (1994); 100 (2000).

(2) H. Valds, J.A. Sordo J. Phys. Chem. A (in press).

(3) H. Valds, J.A. Sordo Chem. Phys. Lett. (in press).

(4) F. Monnat, P. Vogel, R. Meana, J.A. Sordo Angew. Chem. Int. Ed. 42, 3924 (2003).

Accurate interaction energies for hydrogen bonded and stacked structures of DNA bases complete basis set calculations at the MP2 and CCSD(T) levels and comparison with lower-level theoretical methods

Pavel Hobza

Institute of Organic Chemistry and Biochemistry, Acadaemy of Sciences of the Czech Republic
Flemingovo nm. 2, 166 10 Prague 6, Czech Republic

Stabilization energies of planar H-bonded and stacked structures of gas phase optimized and crystal DNA base pairs were determined as the sum of the complete basis set (CBS) limit of MP2 stabilization energies and (?ECCSD(T)- ?EMP2) correction term evaluated with the 6-31G** basis set. The CBS limit was determined by a two-point extrapolation using the aug-cc-pVXZ basis sets for X=D, T and Q. The convergence of the CCSD(T) correction term is known to be faster than that of the MP2 or CCSD(T) correlation energy themselves. Final stabilization energies (in kcal/mol) of the gas-phase optimized DNA base pairs are very substantional (A...T WC, 15.4; mA...mT H, 16.3; A..T stacked, 11.6; mA...mT stacked, 13.1; G...C WC, 28.8; mG...mC WC, 28.5; G...C stacked, 16.9; mG....mC stacked, 18.0), much larger than published previously. On the basis set of comparison with experimental data we conclude that values presented represent the lower boundary of the true stabilization energies. While the H-bonding energies are comparable in crystal and vacuum, the stacking energies are considerably smaller in crystal. Despite this, the stacking is still important and accounts for a significant part of stabilization in crystals of DNA. Hairpin structure is characterized by significant stacking. The DFT/B3LYP method yields satisfactory values of interaction energies for H-bonded structures, while it fails completely for stacking. The PW91 DFT functional matches the accurate H-bonded interaction energies even better with a maximum relative error of 2.3 kcal/mol but this functional fails again completely for stacking. Very good peformance of non-polarizable Cornell et al force field for H-bonding and stacking is confirmed.

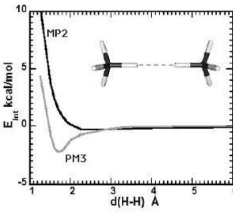
Optimized core-core functions for semiempirical studies on intermolecular interactions

Manuel F. Ruiz-López

Equipe de Chimie et Biochimie théoriques, UMR CNRS-UHP No. 7565, Université Henri Poincaré, Nancy I, BP 239, 54506 Vandoeuvre-lés-Nancy Cedex, France

Manuel.Ruiz@lctn.uhp-nancy.fr

One of the most important shortcomings of primitive semiempirical methods was their inaccuracy in describing intermolecular interactions, in particular hydrogen bonds. Efforts were put forth to overcome this problem and different models were developed. Among them, AM1 and PM3 are the most general and have become the most used nowadays. Though encouraging results have been obtained with these methods some important deficiencies have also been reported. Moreover, nonphysical artifacts have been shown to b present in the potential energy surfaces of some simple complexes that have been related to the presence of Gaussian correction functions (GCF) in the core-core repulsion terms. An example is shown in the Figure, which represents the interaction energy of two methane molecules as a function of the intermolecular H-H distance. The PM3 curve exhibits an energy minimum (2 kcal/mol) for dHH = 1.7 Å. We have recently proposed a scheme that considerably improves the description of interacting molecules (1-3). Basically, the conventional PM3 GCFs are replaced by suitable functions exhibiting the correct physical behavior in the whole range of intermolecular separation distances. These functions are optimized to reproduce high level ab initio results for the interaction potential energy surface of reference systems. In this talk, we shall outline the approach and illustrative results will be presented for 1) the structure of hydrated systems, 2) host-guest interactions, 3) the prediction of diastereoselectivities in asymmetric synthesis.



1)Bernal-Uruchurtu MI, Martins-Costa MTC, Millot C, Ruiz-López MF (2000) J. Comput. Chem., 21: 572-581.

2)Bernal-Uruchurtu MI, Ruiz-López MF (2000) Chem. Phys. Lett., 330: 118-124.

3)Harb W, Bernal-Uruchurtu MI, Ruiz-López MF (2004) Theoret. Chem. Acc., in press

Theoretical Insights in Enzyme Catalysis. Towards a Rational Design of Catalytic Antibodies.

Vicent Moliner, Sergio Martí, Maite Roca, Raquel Castillo, Juan Andrés

Departament de Ciéncies Experimentals; Universitat Jaume I, Box 224, Castellón (SPAIN)
Silvia Ferrer, Iñaki Tuñón, Estanislao Silla Departament de Química Física/ IcMol;
Universidad de Valencia, 46100 Burjasot, (Spain) Juan Bertrán Departament de Química;
Universitat Autónoma de Barcelona,08193 Bellaterra, (Spain) Ian H. Williams Department of
Chemistry; University of Bath. BA2 7AY Bath, (United Kingdom)

Recent computational developments have allowed realistic modelling of chemical processes in biological environments and in particular of enzyme catalysis. From the original Pauling's proposal about the fit between the reaction transition state (TS) and the protein environment, different explanations on the origin of enzymes ability to enhance reaction rates have been given. Thus, while some scientists have focused in the TS stabilization, enzyme catalysis has been also explained by focusing on the reactants structure in the Michaelis complex. All in all, the only real evidence for Pauling's proposal was the fact that stable compounds that resembled the TS, transition state analogs (TSAs), were competitive inhibitors of the enzyme. These stable molecules, TSAs, were pioneering used by Lerner, Schultz, Benkovik and Tramontano as haptens in immunization processes to synthesise new catalysts: the catalytic antibody (CA). The study of the processes associated to the CA activity provides an opportunity to examine and understand enzyme catalysis and vice versa; the in depth knowledge of enzyme activity can be used to improve the specificity, selectivity and efficiency of these new catalysts.

In this talk we will analyse some examples of enzyme catalysis. Using our own results from hybrid Quantum Mechanics / Molecular Mechanics (QM/MM) treatments, we will discuss on the origin of enzyme catalysis and the application of this knowledge to the rational design of catalytic antibodies or the improvement of existing inhibitors.

From Simplified Models to Real Systems: a DFT Approach to Experimental Organometallic Chemistry

Odile Eisenstein

Odile.eisenstein@univ-montp2.fr

Laboratoire de Structure et Dynamique des Systémes Moléculaires et Solides (UMR 5636),
Universit Montpellier 2 , 34095 Montpellier Cedex 5, France

Computational studies of transition metal complexes can now give very useful information to the experimental chemist provided that a robust accurate method is used and that realistic models of the experimental systems are considered. The density functional method is unanimously recognized as a method of choice. We have used the DFT method at the B3LYP or B3PW91 levels. QM/MM method were used for the larger systems. We will focus on the importance of the models for representing the experimental situation. This takes a crucial importance when several weak interactions are present in chemical systems. It will be shown how the nature of ligands, substitutants and counter-ions can determine the structure and behaviour of transition metal complexes. The following points will be addressed: favouring or disfavouring the agostic interaction by ancillary groups, counter-ion role in the structure and fluxional properties of N-hetero-substituted carbene complexes. We will also show how one can take advantage of the QM/MM calculations for interpretations and optimal representation of complexes.

Some References

A. Kovacevic, S. Grndemann, J. R. Miecznikowski, E. Clot, O. Eisenstein, R. H. Crabtree, Chem. Commun. 2002, 2580-1.

J. R. Miecznikowski, S Grndemann, M. Albrecht, C. Mgret, E. Clot, J. W. Faller, O. Eisenstein, R. H. Crabtree, J. C. S. Dalton Trans. 2003, 831-8.

E. Clot, O. Eisenstein, T. Dube, J. W. Faller, and R. H. Crabtree, Organometallics 2002, 21, 575-580.

A.C. Cooper, E. Clot, F. Maseras, O. Eisenstein, K.G. Caulton J. Amer. Chem. Soc, 1999, 121, 97-106.

G. Ujaque, A. C. Cooper, F. Maseras, O. Eisenstein, K. G. Caulton, J. Amer. Chem. Soc. 1998, 120, 361-5.

BONDING, BONDING PERTURBATION AND INTRINSIC REACTIVITY IN GAS PHASE ION-MOLECULE INTERACTIONS.

Otilia Mó

Departamento de Química, C-9. Universidad Autónoma de Madrid. Cantoblanco,
28049-Madrid. Spain.

Substantial dissimilarities can be found in the bonding between a monocation and a neutral compound depending on the characteristics of the former. Besides the electrostatic interactions that are present in all cases, the polarization of the neutral compound can trigger the formation of dative bonds or, when the ion has an extremely large electron affinity, the ionization of the neutral system and its unimolecular fragmentation. Dative bonds are favored, through the participation of low-lying empty 4s and/or 3d orbitals, when the ion is a transition metal singly-charged species. These dative bonds, as well as the back-donation from the lone-pairs of the metal into antibonding orbitals of the neutral, are particularly favored when the neutral has X-H bonds with a high X+d-H-d polarity, or alternatively some kind of unsaturation, or both, explaining, for instance, the very large binding energies of Cu+ to the alkaline and earth-alkaline hydrides and the strong bonding perturbation undergone by the neutral base. The reactions involving halogen cations are paradigmatic examples of limit cases where these bonding perturbations lead to the spontaneous unimolecular fragmentation of the system. This is clearly exemplified by the reactions between vinylsilane and F+(1D, 3P). Finally we shall analyze the importance of coulomb explosions on gas-phase reactions involving Ca2+ metal dications.

DIOXYGEN ACTIVATION AT MONOCOPPER ENZYME SITE MODELS

Benjamin F. Gherman, William B. Tolman, Christopher J. Cramer

Department of Chemistry and Supercomputer Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN, USA.

(cramer@chem.umn.edu)

The activation of molecular oxygen at monocopper centers plays an important role in biology, and in particular with regard to the biosynthesis of neurohormones by the Cu-containing enzymes dopamine β-monooxygenase (DβM) and the peptidylglycine α-hydroxylating monooxygenase (PHM) component of the bifunctional peptidylglycine α-amidating monooxygenase (PAM). In order to gain an understanding of the first stage of the catalysis (i.e. dioxygen activation at the monocopper active sites), 1:1 Cu/O2 adducts coordinated to the biomimetic β-diketiminate and anilido-imine ligands of Tolman and co-workers [1,2] have been studied using a combination of DFT and CASPT2 methods, a protocol which stems from earlier work on closely related systems [3]. In addition, computations have also been carried out on small monocopper coordination complexes, where ligands have been chosen based upon available crystallographic and EXAFS data for DβM and PHM in order to best reproduce the copper coordination environments in those enzymes. Both sets of calculations have focused on characterizing the formation of the adducts, interconversion between side-on and end-on adducts, and properties of the protonated forms of the adducts. These results will form the foundation for subsequent work on OO bond cleavage to potentially yield Cu(III)=O species as well as modeling of the hydroxylation reaction carried out by the Cu/O2 adducts (i.e. the second stage of the DβM and PHM reactions).

(1) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. J. Am. Chem. Soc. 2002, 124, 2108-2109.

(2) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. J. Am. Chem. Soc. 2002, 124, 10660-10661.

(3) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L. Proc. Natl. Acad. Sci. U. S. A. 2003, 100, 3635-3640.

Quantum calculations of reaction rates and the conformations of biomolecules

David C. Clary

Department of Physical and Theoretical Chemistry University of Oxford South Parks Road
Oxford OX1 3QZ

email: david.clary@chem.ox.ac.uk

This lecture will describe two pieces of research recently carried out in our group at the University of Oxford.

The first topic will be the description of a general reduced dimensionality method that combines accurate quantum chemistry calculations of a small number of key points on the potential energy surface with a quantum-dynamical treatment of the bonds being broken and formed in a chemical reaction. Recent applications of the method, by Dr Boutheina Kerkeni in our group, to the reactions of H atoms with polyatomics such as CH4, C2H6 and CH3OH will be described. The results demonstrate significant tunnelling in these reactions and the calculated rate constants compare favourably with experiment. The promising results suggest that this will be a general procedure for making accurate predictions on the reaction kinetics and dynamics of larger polyatomic molecules.

We will also report on our recent development of a torsional path integral method for predicting the structures of biomolecules. This method allows for quantum calculations of free energies of biomolecules for finite temperatures. Recent applications by Tommy Miller in our group on predicting conformational preferences in glycine and a nor-adrenaline analogue will be described and compared with experiment. The results show the importance of the quantum anharmonic entropy in determining the structures of these biomolecules.

INCLUDING ELECTRONS IN COMPLEX MOLECULAR SYSTEMS.

Massimiliano Aschi[a], Andrea Amadei[b], Alfredo Di Nola[c]

[a]Universita' di L'Aquila - Italia

[b]Universita' di Roma 'Tor Vergata' - Italia

[c] Universita' di Roma 'La Sapienza' - Italia

What is a complex molecular system ? Many definitions can be proposed for addressing this question. By a mechanical-statistical point of view the complexity of a system is to be quantified on the basis of the accessibility of its configurational space. Therefore any significant modelization of a complex system can be carried out in the framework of classical molecular theories in which the exhaustive statistical sampling is allowed by the mathematical simplicity of the physical model. Of course, within this 'molecular view', any informations concerning the electrons are lost. For this reason in the last decade many efforts have been made for trying to re-include the electronic degrees of freedom in systems containing a large number of atoms. In this respect we have proposed and applied a new computational method, the Perturbed Matrix Method, whose underlying philosophy is the inclusion of the electrons in a phase-space sampling in order to obtain equilibrium electronic properties, e.g. spectroscopic properties, for large biomolecular systems and condensed (liquid) states. In this talk the main theoretical features of the method will be outlined and some examples illustrated.

EXCITED STATE DYNAMICS IN COMPLEX SYSTEMS

Cosimo Ciminelli, Giovanni Granucci, Maurizio Persico, Alessandro Toniolo

Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, v. Risorgimento 35,
I-56126 Pisa (Italy)

e-mail: mau@dcci.unipi.it

We have set up a semiclassical strategy based on surface hopping for the simulation of nonadiabatic dynamics of excited states. We determine electronic energies and wavefunctions "on-the-fly" by a semiempirical method: the wavefunctions are of the CI type, and are based on MO's generated by a floating occupation SCF. In this way we can represent homolytic bond breaking, orbital degeneracies and other cases where a multiconfigurational treatment is required [1-3]. The method lends itself to the search of minima and optimal intersection points in the PES [4]. We have coupled our semiempirical method with a force-field description of the chemical environment, i.e. we have implemented a hybrid QM/MM method that enables us to represent state-specific environmental effects, such as solvation or adsorption on solid surfaces [5]. The method has already been used to characterize conical intersections in solution [6]. A further step consisted in adapting Antes and Thiel's "connection atom" approach, to treat covalent bonding between the QM and MM susbsystems. In this way we can simulate the dynamics of supramolecular systems, such as choromophores belonging to biological macromolecules [7]. Examples of application will concern the photoisomerization of azobenzene [3] and of its derivatives. One of the goals is to simulate the photoswitching of the double cyclopeptide with azobenzene bridge shown in figure, from the cis intramolecularly hydrogen-bonded isomer to the trans self-assembling form.

[1] G. Granucci, M. Persico, A. Toniolo, J. Chem. Phys. 114, 10608 (2001)

[2] A. Toniolo, G. Granucci, S. Inglese, M. Persico, PCCP 3, 4266 (2001)

[3] C. Ciminelli, G. Granucci, M. Persico, Chem. Eur. J. 10, 2327 (2004)

[4] A. Toniolo, M. Ben-Nun, T. J. Martnez, J. Phys. Chem. A 106, 4679 (2002)

[5] M. Persico, G. Granucci, S. Inglese, T. Laino, A. Toniolo, THEOCHEM 621, 119 (2003) [6] A. Toniolo, G. Granucci, T. J. Martnez, J. Phys. Chem. A 107, 3822 (2003) [7] A. Toniolo, C. Ciminelli, G. Granucci, T. Laino, M. Persico, Theoret. Chem. Acc. 93, 270 (2004)

Statically Screening Potential. Modeling Weakly Bound Plasma Environments

Cecilia Sarasola, Jose M. Mercero, Xabier Lopez and Jesus M. Ugalde

Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072, 20080 Donostia, Euskadi (Spain)

The properties of the statically screening interaction potential will reviewed and its usability for the modeling of a class of screening effects will be highlighted. The experiment of Bell et al.[1] will be discussed to emphasized that screening effects are highly dependent on the actual electronic state of the system considered. Afterwards, a molecular orbital theory implementation for systems with statically screened interparticle interactions will be outlined and some of the properties of the resulting wave function presented. These include, the virial theorem and the electron-nucleus and the electron-electron cusp conditions.

Finally, the performance of the model will be illustrated with aid of the following two-electron systems: H^-, the Positronium anion Ps^-, He and H2. Then, the atomic oxidation states as a function of the screening strength will be discussed. Next will be move on the analysis of polyelectron atomic excited states and resonances in H^- and He^-. Also, the plasma pressure induced shifts of the electronic transitions will be presented.

References:

1. *Evidence for dynamical screening of projectiles ions passing through solids.* F. Bell, H. D. Betz, H. Panke and W. Stehling, J Phys B. 9, L443 (1976)

2. *Bound electronic states of the statically screened electric-dipole.* J.M. Ugalde and C. Sarasola; Phys. Rev. A. 54, 2868 (1996)

3. *Evaluation of screened nuclear attraction and electron repulsion molecular integrals over gaussian basis functions.* J.M. Ugalde, C. Sarasola; Int. J. Quantum Chem. 62, 273 (1997).

4. *Transition energies and emission oscillator strengths of helium in model plasma environments.* X. Lopez, C. Sarasola and J.M. Ugalde; J. Phys. Chem. A. 101, 1804 (1997).

5. *Atomic and molecular bound ground states of the Yukawa potential.* J.M. Ugalde, C. Sarasola, X. Lopez; Phys. Rev. A 56, 1642 (1997).

6. *Bound excited states of H^- and He^- in the statically screened coulomb potential.* J.M. Mercero, J.E. Fowler, C. Sarasola, J.M. Ugalde; Phys. Rev. A 57, 2550 (1998).

7. *On the oxidation state of the guest atom of metallofullerene endohedral complexes.* C. Sarasola, J.M. Elorza, J.M. Ugalde; Chem. Phys. Lett. 285, 226 (1998).

8. *Cusp conditions for non-coulombic interactions.* Iñaki Silanes, Jesus M. Ugalde, Russell J. Boyd; J. Mol. Struct. (Theochem), 527, 27 (2000). (Vedene H. Smith, Jr. Festschrift)

9. *Atomic charge states in a weakly coupled plasma environment.* I. Silanes, J. M. Mercero, J.M. Ugalde; Phys. Rev. E. 66, 026408 (2002)

Results and future directions

The spanish theoretical chemistry community has experienced a great advance during the last two decades in Spain. This growing activity has been motivated, in part, by the intense docent and research work of a group of outstanding scientists working in this field at several Universities and Research Centres (CSIC mainly), as well as by the huge increment of computational resources during the same period. On the other hand, the increasing demand in the field of Chemistry, Physics, Biology and Pharmacy of computational tools has attracted the development of new hybrid theoretical-experimental approaches. Particularly interesting is the possibility of complementarities between theoretical and experimental studies (spectroscopic, thermodynamic, kinetic, electrochemist, etc...) allowing a more global and deep perspective of the chemical problems. Actually there are more than 25 Universities in Spain where there exist consolidated groups in the various special fields.

This workshop intended to be an incentive for the participation of PhD students from the different Spanish and European groups, and to do that we will offer grants covering different aspects to attend the conference. During the first workshop of this series, held in Miraflores de la Sierra (Madrid-1998), the idea was proposed to elaborate an inter-universitary PhD program. That initiative turned out to be fruitful and became reality when in 1999 the National Spainish PhD program in Theoretical and Computational Chemistry started, involving 12 Universities. For the present or past students following these PhD program on Theoretical and Computational Chemistry, the conference ESPA2004 constituted an opportunity to know from first hand the more recent tendencies and, for mostly of them, has been the first international conference that they attend.

We think that, in addition to the specific scientific value of the workshop, this workshop fulfilled a very important educational goal for the formation of new researchers in the field. The next edition of this ESPA series of workshops, V-ESPA-2006, will be held in 2006 in Santiago de Compostela (Spain).

Espa-2004 timetable

Tuesday, 14th		
16:30-20:00		Registration
20:00-20:30		Opening Session
20:30		Welcome Reception
Wednesday, 15th		
Chair: S. Olivella		
9:00-09:45	R. J. Bartlett	*Ab Initio DFT: Problems and Prospects*
9:45-10:30	A. M. J. Sánchez	*Reduced Scaling in Theoretical Chemistry Using Cholesky decomposition*
10:30-11:00		Coffe Break
Chair: E. Ludeña		
11:00-11:4	G. E. Scuseria	*Recent progress in the development of exchange-correlation functionals*
11:45-12:30	J. M. Soler	*Exchange and correlation as a functional of the local density of states*
12:30-13:15	A. D. Becke	*Post-Hartree-Fock Correlations functionals*
13:15-15:00		Lunch Break
Chair: F. Muñoz		
15:00-15:45	G. Borstel	*Large scale computer modeling of point defects in perovskite crystals*
15:45-16:30	E. Kotomin	*First principles calculations of the atomic and electronic structure and reactivity of ABO_3 perovskite surfaces*

16:30-16:45		Coffe Break	.
16:45-18:15		Poster session A	.
18:45-20:00		Visit to the Sculpture Museum	.

Thursday, 16th

Chair: S. Vázquez			
9:00-09:45	M. Solá	*Aromaticity quantified from the atoms in molecules delocalization indices*	
9:45-10:30	P. Pyykkö	*New predicted heavy-element species*	
10:30-11:00		Coffe Break	.
Chair: E. Sánchez			
11:00-11:4	J. A. Sordo	*Why Study Weakly-Bound Systems*	
11:45-12:30	P. Hobza	*Accurate interaction energies for hydrogen bonded and stacked structures of DNA bases*	
12:30-13:15	M. F. Ruiz-López	*Optimized Core-Core Functions for Semiempirical Studies on Inteemolecular Interactions*	
13:15-15:00		Lunch Break	.
Chair: L.A. Eriksson			
15:00-15:45	V. Moliner	*Theortical Insights in Enzime Catalysis. Toward a Rational Design of Catalytic Antibodies*	
15:45-16:30	O. Einsestein	*From Simplified Models to Real Systems: a DFT Approach to Experimental Organometallic Chemistry*	
16:30-16:45		Coffe Break	.
16:45-18:15		Poster session B	.

Friday, 17th

Chair: S. Caballol			
9:00-09:45	O. Mó	*Bonding, bonding perturbation and Intrinsic reactivity in Gas Phase Ion-Molecule Interactions*	
9:45-10:30	C. J. Cramer	*Dioxygen Activation at Monocopper Enzyme Site Models*	
10:30-11:00		Coffe Break	.
Chair: W. C. Herndon			
11:00-11:4	D. C. Cleary	*Quantum calculations of reaction rates and the conformation of biomolecules*	
11:45-12:30	M. Aschi	*Including electrons in complex molecular systems*	
12:30-13:15	M. Pérsico	Excited State dynamics in Complex Systems	
13:15-15:00		Lunch Break	.
Chair: I. Nebot-Gil			
15:00-15:45	J. M. Ugalde	*Statically Screening Potential. Modeling Weakly Bound Plasma Environments*	
15:45-16:30	J. Bertran	*Summary Remarks*	
16:30-21:30		Visit to Peñafiel Castle	.

21:30-24:00 Conference Dinner .

LIST OF PARTICIPANTS

Aguado, Andrés, Universidad de Valladolid, aguado@metodos.fam.cie.uva.es
Aguado, Edurne, Universidad del País Vasco, qfbagcam@lg.ehu.es
Aguilar, Manuel Ángel, Universidad de Extremadura, maguilar@unex.es
Alcami, Manuel, Universidad Autónoma de Madrid, manuel.alcami@uam.es
Alonso, Jose L., Universidad de Valladolid, jlalonso@qf.uva.es
Alonso, Julio A., Universidad de Valladolid, jaalonso@fta.uva.es
Alonso, Mercedes, Instituto Química Orgánica (CSIC), mercuea@iqog.csic.es
Alvarez Blanco, Miguel, Universidad de Oviedo, miguel@carbono.quimica.uniovi.es
Alvarez, Jose Ramon, Universidad Autonoma de Madrid, alvarez.collado@uam.es
Alvariño, José María, Universidad de Salamanca, alva@usal.es
Andrés, Juan M., Universitat Jaume I, andres@exp.uji.es
Anglada Rull, Josep M., CSIC, anglada@iiqab.csic.es
Aramburu-Zabala, Antonio, Universidad de Cantabria, aramburj@unican.es.
Arenas Hinojosa, Pedro Nilo, Universidad de Cádiz, manuel.fernandez@uca.es
Aschi, Massimiliano, Universita' di L'Aquila, m.aschi@caspur.it
Ayala, Regla, Universidad de Sevilla, regla@simulux.us.es
Balbás, Luis Carlos, Universidad de Valladolid, balbas@lcb.fam.cie.uva.es
Barrientos, Carmen, Universidad de Valladolid, cbb@qf.uva.es
Bartlett, Rodney J., University of Florida, bartlett@qtp.ufl.edu
Becke, Axel D., Queen's University, becke@chem.queensu.ca
Bertrn, Juan, Universitat Autnoma de Barcelona, bertran@klingon.uab.es
Bidon-Chanal Badia, Axel, Universitat de Barcelona, gotlob@far1.far.ub.es
Borstel, Gunnar, University of Osnabrck, gborstel@rz.uni-osnabrueck.de
Bustos Martín, Enrique, Universidad de Valladolid, ebustos@qf.uva.es
Cabaleiro, Enrique M,. Universidade de Santiago de Compostela, qftkike@usc.es
Caballol, Rosa, Universitat Rovira i Virgili, caballol@quimica.urv.es
Calzado, Carmen J., Universidad de Sevilla, calzado@us.es
Campomanes, Pablo, Universidad de Oviedo, pcramos.uo@uniovi.es
Cardenas, Gloria I., Universidad de Santiago de Chile, gcardena@lauca.usach.cl
Chang, Chun-Ming, National Dong Hwa University, cmc@mail.ndhu.edu.tw
Cimas, lvaro, Universidad de Valladolid, acs@qf.uva.es
Clary, David C., University of Oxford, david.clary@chem.ox.ac.uk
Contreras García, Julia, Universidad de Oviedo, julia@carbono.quimica.uniovi.es
Corbacho, Elizabeth, Universidad de Sevilla, eli@simulux.us.es
Cornejo, Alfonso, Universidad Pblica de Navarra, alfonso.cornejo@unavarra.es
Costales, Aurora, Universidad de Oviedo, yoyi@carbono.quimica.uniovi.es
Cramer, Christopher, University of Minnesota, cramer@chem.umn.edu
Cruz Hernndez, Norge, University of Sevilla, norge@us.es

Díaz Fernández, Natalia, Universidad de Oviedo, diazfnatalia@uniovi.es
Díaz-Tendero, Sergio, Universidad Autónoma de Madrid, sergio.diaztendero@uam.es
Dobado, José A., Universidad de Granada, dobado@ugr.es
Dominguez-Gomez, Rosa, U. Politcnica de Madrid, rdominguez@op.upm.es
D'Oria, Emiliana, Universitat de Barcelona, e.doria@qf.ub.es
dos Santos, Daniel, Örebro University, daniel.dos-santos@nat.oru.se
Eisenstein, Odile, Universit Montpellier 2, Odile.eisenstein@univ-montp2.fr
Eriksson, Leif A., Örebro University, leif.eriksson@nat.oru.se
Estévez, Carlos Manuel, Universidade de Vigo, cestevez@uvigo.es
Fernández, Eva María, Universidad de Valladolid, eva@lcb.fam.cie.uva.es
Fernández, Jorge A., URV, jafd@fq.urv.es
Fernández, Julio Juan, Universidad Politcnica de Madrid, julio@etsit.upm.es
Fernández, Jorge, Universidad Atnoma de Madrid, j.fernandez@uam.es
Fernández, Antonio, Universidade de Santiago de Compostela, qftramos@usc.es
Francisco, Evelio, Universidad de Oviedo, angel@fluor.quimica.uniovi.es
Frau, Juan, Universidad de las Islas Baleares, juan.frau@uib.es
Gamallo, Pablo, U. Barcelona y C. de Recerca en Química Teórica, gamallo@qf.ub.es
García, Ernesto, Universidad del País Vasco, qfpgapae@vc.ehu.es
García Fernández, Pablo, Universidad de Cantabria, garciapa@unican.es
Garcías Llabrs, Rafael Carlos, Universitat de eles Illes Balears, rafel.garcias@uib.es
Glossman, Daniel, Grupo QCOSMO - CIMAV, daniel.glossman@cimav.edu.mx
Godinho, Sofia S. M. C., Universidade de Lisboa, sgodinho@itqb.unl.pt
Gomez, Isabel, Universitat Rovira i Virgili, gomez@quimica.urv.es
Gonzalez-Garcia, Nuria, Universitat Autonoma de Barcelona, nuria@qf.uab.es
Gracia, Lourdes, Universidad Jaume I, lgracia@exp.uji.es
Graciani Alonso, Jess, Universidad de Sevilla, graciani@us.es
Graa, Ana M., Universidade de Vigo, ana@uvigo.es
Henry, William, Dublin City University, william.henry2@mail.dcu.ie
Hermida Ramón, Jose Manuel, Universidade de Vigo, jose-hermida@uvigo.es
Herndon, William C., University of Texas at El Paso, wherndon@utep.edu
Hobza, Pavel, Acadaemy Sciences Czech Republic, pavel.hobza@uochb.cas.cz
Huertas, Oscar, Universitat de Barcelona, oscar@far1.far.ub.es
Junquera-Hernndez, José Miguel, Universidad de Valencia, jose.m.junquera@uv.es
Kotomin, Eugene, Max Planck Institut FKF, kotomin@fkf.mpg.de
Largo, Antonio, Universidad de Valladolid, alargo@qf.uva.es
Lavín, Carmen, Universidad de Valladolid, clavin@qf.uva.es
Lopez, Xabier, Euskal Herriko Unibertsitatea, poplopex@sq.ehu.es
López, María J., Universidad de Valladolid, maria@lab2.fam.cie.uva.es
López, Ramn, Universidad de Oviedo, rlopez@uniovi.es
Ludeña, Eduardo, Euskal Herriko Universitatea, eludena@ivic.ve
Luque, F. Javier, Universitat de Barcelona, javier@far1.far.ub.es
Mandado, Marcos, Universidade de Vigo, mandado@uvigo.es
Maresca, Olivier, Universitat Autnoma de Barcelona, olivier@klingon.uab.es

Márquez Cruz, Antonio M., Universidad de Sevilla, marquez@us.es
Martín, Inmaculada, Universidad de Valladolid, imartin@qf.uva.es
Martín Pends, ngel, Universidad de Oviedo, angel@fluor.quimica.uniovi.es
Martínez, Jose Manuel, Universidad de Sevilla, josema@us.es
Martínez García, M del Henar, Universidad de Valladolid, henar@eis.uva.es,
Martínez Nez, Emilio, Universidade de Santiago de Compostela, qfemilio@usc.es
Martorell Masip, Benjamí, Universitat Rovira Virgili, bmm@quimica.urv.es
Massó González, Helena, DAMIR/IEM/CSIC, masso@damir.iem.csic.es
Matxain, Jon Mattin, Euskal Herriko Unibertsitatea, pobmabej@sq.ehu.es
Mayor Rueda, Esteban, Universidad de Valladolid, emayor@qf.uva.es
Meana Pañeda, Rubén, Universidad de Oviedo, rmeana.uo@uniovi.es
Mediavilla, César, Universidad Complutense de Madrid, cmm@quim.ucm.es
Melchor, Santiago, Universidad de Granada, smelchor@ugr.es
Menéndez, M Isabel, Universidad de Oviedo, isabel@uniovi.es
Menéndez Montes, Jose Manuel, Universidad de Valladolid, mamel@qf.uva.es
Mercero, Txema, UPV/EHU, pobmelat@sc.ehu.es
Mó, Otilia, Universidad Autónoma de Madrid, otilia.mo@uam.es
Moles Tena, Pamela, Universitat Jaume I de Castellón, pmoles@guest.uji.es
Molina Martín, Luis Miguel,, Universidad de Valladolid, molina@phys.au.dk
Moliner, Vicent, Universitat Jaume I, moliner@exp.uji.es
Montero-Campillo, M.Merced, Universidade de Santiago, qfmerche@usc.es
Mujika, Jon Iaki, UPV/EHU, pobmugoj@sc.ehu.es
Muñoz, Francisco, Universidad de las Islas Baleares, dqufmi0@uib.es
Muñoz-Caro, Camelia, Universidad de Castilla-La Mancha, quimcom@uclm.es
Nebot-Gil, Ignacio, Universitat de Valencia, Ignacio.Nebot@uv.es
Niño, Alfonso, Universidad de Castilla-La Mancha, quimcom@uclm.es
O'Boyle, Noel, Dublin City University, oboylen2@mail.dcu.ie
Ochando Pardo, Montserrat, Universitat de Valéncia, Montserrat.Ochando@uv.es
Olivella, Santiago, CSIC, sonqtc@iiqab.csic.es
Omar Seida, Salama, Universidad Autónoma de Madrid, salama.omar@uam.es
Ordejón, Belén, Universidad Autónoma de Madrid, belen.ordejon@uam.es
Ortí, Enrique, Universidad de Valencia, enrique.orti@uv.es
Oviedo López, Jaime, Universidad de Sevilla, jol@us.es
Palacios, Pablo, Universidad Politcnica de Madrid, pablop@etsit.upm.es
Paz, Óscar, Universidad Autónoma de Madrid, oscar.paz@uam.es
Peláez Ruiz, Daniel, Universidad de Málaga, dpr@uma.es
Peña-Gallego, Angeles, Universidad de Santiago, qfpena@usc.es
Pérez-Romero, Encarnación, Universidad de Salamanca, epromero@usal.es
Persico, Maurizio, Universita di Pisa, mau@dcci.unipi.it
Poater, Jordi, Universitat de Girona, jordi.poater@udg.es
Pou-Amérigo, Rosendo, Universitat de Valncia, rosendo.pou@uv.es
Pyykkö, Pekka, University of Helsinki, pekka.pyykko@helsinki.fi
Queralt, Núria, Universitat Rovira i Virgili, nqr@quimica.urv.es

Ramírez, Víctor Miguel, Universidad de Valencia, victor.Ramirez@uv.es
Rayón Rico, Víctor Manuel, Universidad de Valladolid, vmrr@qf.uva.es
Redondo, Pilar, Universidad de Valladolid, predondo@qf.uva.es
Reguero, María del Mar, Universitat Rovira i Virgili, reguero@quimica.urv.es
Reyes, Sebastián, Universidad de Castilla-La Mancha, Sebastian.Reyes@uclm.es
Rezabal, Elixabete, Euskal Herriko Unibertsitatea, pobrease@sq.ehu.es
Riviére, Paula, Universidad Autónoma de Madrid, paula.riviere@uam.es
Roca Moliner, Maite, Universitat Jaume I, mroca@exp.uji.es
Rodríguez, Luis, Universitat Autnoma de Barcelona, luis@klingon.uab.es
Rodríguez, Manuel Aurelio, Universidad del País Vasco, qfbroloa@vc.ehu.es
Rodriguez-Otero, Jesus, Universidad de Santiago, qftjesus@usc.es
Romo, Susana, URV, srda@fq.urv.es
Ruipérez, Fernando, Universidad Autónoma de Madrid, fernando.ruiperez@uam.es
Ruiz Nieto, Luis Felipe, Universidad Autónoma de Madrid, luis.ruiz@uam.es
Ruiz-López, Manuel, Université Henri Poincaré, Manuel.Ruiz@lctn.uhp-nancy.fr
Russo, Nino, Universit della Calabria, nrusso@unical.it
San Román, Ma Luisa, Universidad Autónoma de Morelos, maluisaz@buzon.uaem.mx
San Sebastián, Eider, University of the Basque Country, qpbsalae@sq.ehu.es
Sánchez de Mers, Alfredo M.J., Universidad de Valencia, alfredo.Sánchez@uv.es
Sánchez Marcos, Enrique, Universidad de Sevilla, sanchez@simulux.us.es
Sánchez Mrquez, Jesús Universidad de Cádiz, jesus.sanchezmarquez@uca.es
Sánchez-González, Angel, Universidad de Granada, angels@ugr.es
Sancho, Juan C., Service de Chimie des Materiaux Nouveaux, jc.sancho@averell.umh.ac.be
San-Miguel, Miguel, Universidad de Sevilla, smiguel@us.es
Sanz, Javier Fdez., Universidad de Sevilla, sanz@us.es
Scuseria, Gustavo E., Rice University, guscus@rice.edu
Senent, Maria Luisa, DAMIR-IEM-CSIC, imts420@iem.cfmac.csic.es
Sicilia, Emilia, Universiá della Calabria, siciliae@unical.it
Sicilia, M del Carmen, Universidad de Castilla-La Mancha, mariacarmen.sicilia@uclm.es
Silanes, Iaki, UPV/EHU, poasicri@sq.ehu.es
Sodupe, Mariona, Universitat Autonoma Barcelona, mariona@klingon.uab.es
Solá, Miquel, Universitat de Girona, miquel@stark.udg.es
Solans Monfort, Xavier, Universit Montpellier II, solans@univ-montp2.fr
Soler, José M., Universidad Autónoma de Madrid, jose.soler@uam.es
Sordo, José A., Universidad de Oviedo, jasg@uniovi.es
Soteras, Ignacio, Universitat de Barcelona, ignacio@far1.far.ub.es
Sousa Romero, Carmen, Universidad de Barcelona, c.sousa@qf.ub.es
Suárez, Dimas, Universidad de Oviedo, dimas@uniovi.es
Taratiel, David Universitat Rovira i Virgili, dtf@qumica.urv.es
Tel, Luis M., Universidad de Salamanca, lmt@usal.es
Torres, Begoña Universidad de Burgos, begonia@ubu.es
Tortajada, José, Universidad Complutense de Madrid, jtp@quim.ucm.es
Trujillo, Cristina, Universidad Autónoma de Madrid, cristina.trujillo@uam.es

Ugalde, Jesus M., Euskal Herriko Unibertsitatea, ugalde@sq.ehu.es
Valdes, Haydee, Academy Sciences Czech Republic, valdes.gonzalez@uochb.cas.cz
Varela lvarez, Adrián, Universidad de Oviedo, a-varela@telefonica.net
Vázquez Rodríguez, Saulo, Universidade de Santiago de Compostela, qfsaulo@usc.es
Velasco, Ana María, Universidad de Valladolid, amvelasco@qf.uva.es
Vidal, Isaac, Universidad de Granada, isvida@ugr.es
Vila Vilario, Antonio, Universidad de Vigo, vila@uvigo.es
Villa Villa, María, U. Autónoma Metropolitana de Mexico, mvv@xanum.uam.mx
Villar Becares, Raquel, Universidad Pública de Navarra, raquel.villar@unavarra.es
Wahnón, Perla, Universidad Politécnica de Madrid, perla@etsit.upm.es
Yánez, Manuel, Universidad Autónoma de Madrid, manuel.yanez@uam.es

4.2 ESF Psi-k Programme Workshop/Conference Announsements

4.2.1 XII INTERNATIONAL WORKSHOP ON COMPUTATIONAL PHYSICS AND MATERIALS SCIENCE: TOTAL ENERGY AND FORCE METHODS

13-15 January 2005, Trieste (Italy)

Registration form is downloadable from the WEB page:

`http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?email=0&ida=a04178`

where detailed information can be found. Also, you can refer to:

`http://www.democritos.it/events/totalenergy-XII.php`

A preliminary program of the event will be posted at these webpages.

Travel support from National Science Foundation is available for young scientists from US Universities. See the attached advertisement below.

Also, we would like to inform you that during the week 17 - 21 January 2005 DEMOCRITOS-Modeling Center for Research in Atomistic Simulation, INFM, Trieste (Italy), in collaboration with ICTP, Trieste, is organizing a ”Tutorial on the Ab-Initio Simulation of the Electronic, Structural and Dynamical Properties of Materials: a hands-on introduction to the ESPRESSO package (PWscf-FPMD-CP)”.

`Check http://www.democritos.it/events/espresso-tutorial.php`

for relevant information.

Giulia Galli,
Emilio Artacho,
Andrea Dal Corso

Organizers:

”12th Workshop on Computational Physics and Materials Science: Total Energy and Force Methods”, Trieste, Italy, January 13-15, 2005.

How to obtain travel support from National Science Foundation:

The US National Science Foundation has funded the Materials Computation Center (MCC) at the University of Illinois to administer a program to support travel to European computational condensed matter workshops and schools, in particular PSIK and CECAM activities, for scientists from US Universities who could not otherwise attend. A particular focus is on junior scientists (i.e. students, post-docs and assistant professors) or scientists from under-represented groups and institutions.

Check http://www.mcc.uiuc.edu/travel/

for details and application procedures.

The MCC is accepting applications for travel support for the workshop ”Computational Physics and Material Science Total Energy and Force Methods” to be held at the ICTP in Trieste, Italy, Jan. 13-15, 2005.

The deadline for application to the workshop and for travel support is Monday, Nov. 15, 2004.

The MCC expects also to support travel to the PSIK 2005 Conference (http://www.fyslab.hut.fi/psik2005) in Schwaebisch Gmuend, Germany to be held Sept. 17-21, 2005. Applications will be due in early summer 2005.

5 General Workshop/Conference Announcements

5.1 DFG/NANOQUANTA Workshop in Berlin

ORBITAL FUNCTIONALS FOR EXCHANGE AND CORRELATION: THE OPTIMIZED EFFECTIVE POTENTIAL AND RELATED METHODS

March 11-13, 2005

House Christopherus, Berlin, Germany

Organized by:
S. Kurth, E.K.U. Gross (Freie Universitaet Berlin)
H. Ebert (Ludwig-Maximilians-Universitaet Muenchen)

During the last decade the Optimized Effective Potential Method (OPM) evolved into a very attractive and powerful technique in electronic structure calculations of molecules and solids. Based on Density Functional Theory, but going beyond the Local Density Appoximation, it allows to consistently take into account exact exchange as well as controllable approximations for electron-electron correlations.

The aim of the workshop is to bring together researchers developing and applying the OPM and related approaches, such as the GW approximation, SIC and LDA+U methods, to share recent developments. The workshop will deal, in particular, with various approximations for electron-electron correlations, relativistic extensions of the method as well as applications to a wide class of materials including metals and magnetic solids.

The workshop will be held at the House Christopherus in Berlin-Spandau. The price for accomodation and meals (full board) is 185,- Euros for the whole period and has to be paid directly to the hotel by each participant. There is no additional conference fee. Limited financial support is available upon request.

Deadline for registration and abstract submission is January 31, 2005.

More detailed information on the workshop, including a tentative list of speakers, can be found at the workshop web site:

`http://www.physik.fu-berlin.de/~ag-gross/oep-workshop/index.html`

Contact: oep-workshop@physik.fu-berlin.de

5.2 36th Spring School 2005: Magnetism goes Nano

Forschungszentrum Juelich, Germany

February 14-25, 2005

We would like to draw your attention to the

36th Spring School 2005: Magnetism goes Nano (Electron Correlation, Spin Transport, Molecular Magnetism)

which takes place February 14-25, 2005 at the Forschungszentrum Juelich, Germany.

The Forschungszentrum Juelich has a long tradition in organizing these spring schools, which covered over the years a large spectrum of active subjects in condensed matter research. The lecture focus particularly on students and PhD students in physics and related areas, such as chemistry and material science.

There is no conference fee and the book which goes with the lectures is free of charge. Low-cost accomodation has been arranged at the youth hostel in Aachen. The fee is 320 Euro including breakfast and dinner.

Deadline for Registration: December 3, 2004

More information can be found under:

http://www.fz-juelich.de/iff/fs2005

Dr. Stefan Blügel
Director of Theory I
Professor of Physics
Institut für Festkörperforschung (IFF)
Forschungszentrum Jülich
D-52425 Jülich, Germany
Tel.: +49-2461-61-4249
Fax.: +49-2461-61-2850
email: theorie1@fz-juelich.de

Secretary: Ute Winkler
Tel.: +49-2461-61-3136

Internet: `http://www.fz-juelich.de/iff/staff/Bluegel_S`

http://www.planewave.de

6 General Job Announcements

PhD Studentship at Ecole Polytechnique Federale de Lausanne, Switzerland

A PhD position on computer modelling of metal clusters supported by oxide surfaces is immediately available at IRRMA (Institut Romand de Recherche Numerique en Physique des materiaux), a center of excellence in computational condensed matter physics located on the campus of EPFL (Ecole Polytechnique Federale de Lausanne), Switzerland. Cluster properties and their modifications induced by the substrate will be studied with first-principles simulations based on density functional theory and the pseudopotential method.

Candidates should have a degree in Physics, Chemistry or related discipline. A background in density functional theory and experience in ab-initio computations will be elements of preference.

Prospective applicants should send their CV and letters of recommendation to:

Zeljko Sljivancanin (Zeljko.Sljivancanin@epfl.ch)

or

Alfonso Baldereschi (Alfonso.Baldereschi@epfl.ch).

Postdoctoral Position

First-Principles/Multiscale Modeling of Aluminum Alloys

Ford Motor Company/Penn. State University

NSF Postdoctoral Research Associate

A new postdoctoral research position is open for an exciting multidisciplinary program involving multiscale materials modeling. The program involves a team of investigators at the Ford Research Laboratory, Penn St. University, and the National Institute of Standards and Technology (NIST). The postdoctoral research associate should have specific experience with first-principles methods and computational materials science. The associate will strongly interact with our team, consisting of a broad range of scientists with expertise in the modeling areas of first-principles (Dr. C. Wolverton, Ford), computational thermodynamics (Prof. Z.-K. Liu, Penn St.), phase-field microstructural modeling (Prof. L.-Q. Chen, Penn St.), and finite element property prediction (Dr. S. Langer, NIST), as well as computer scientists and mathematicians. The program will be focused on technologically important multicomponent Al alloy systems. Although the official hire will be at Penn State, the researcher will be located at the Ford Research Laboratory in Dearborn, Michigan. Initial appointment will be for one year, and may be renewed up to three years annually, upon mutual agreement. To apply, please immediately send a copy of your resume and names of three references to:

Dr. Chris Wolverton
Ford Motor Company
MD3028/SRL, P. O. Box 2053
Dearborn, Michigan 48121-2053
cwolvert@ford.com

Clarifications or further details can be obtained via e-mail to cwolvert@ford.com.

Penn State University is an equal opportunity employer.

POSTDOCTORAL POSITIONS IN LAWRENCE BERKELEY NATIONAL LAB

POSITION SUMMARY: The scientific computing group at computational research division at LBNL has one or two immediate opening for Postdoctoral Fellows in nanoscale electronic structure calculations. These positions are funded by DOE nanoscience initiatives. Close collaboration with experimental groups at Lawrence Berkeley National Laboratory and UC Berkeley is expected. We use large parallel machines at NERSC (http://www.nersc.gov), one of the largest civilian research computer center in the United States. The scientific computing group (http://hpcrd.lbl.gov/html/SCG.html) is a diverse group working on various aspects of scientific computation. More information about our research activities can be found at `http://crd.lbl.gov/~linwang`.

DUTIES: Work with Dr. Lin-Wang Wang in (1) electronic structure calculations of various nanostructures (colloidal quantum dots, conjugated polymers, electronic levels and transports); (2) methodology developments for large scale nanosystem electronic structure calculations (e.g, charge patching methods, polarizations, impurities and transports).

QUALIFICATIONS: A Ph.D degree in physics or related fields. Experience in electronic structure calculations and programming skills.

NOTES: This is a one year term position with the posibility of renewal for up to three years. LBNL offers very competitive salary for post-doctoral positions.

Interested person should send curriculum vitae and 2-3 recommendation letters to:

Dr. Lin-Wang Wang
Lawrence Berkeley Lab
1 Cyclotron Road
Mail stop 50F
Berkeley, CA 94720
lwwang@lbl.gov

LBNL is an equal opportunity/affirmative action employer.

Post-doctoral position in Theoretical Chemistry

Physical Chemistry Institute of the University of Zurich, Switzerland

Applications are invited for a postdoctoral position in the group of Prof. Juerg Hutter at the Physical Chemistry Institute of the University of Zurich (http://www.unizh.ch/pci). The position is available starting from January 2005 for a period of one year, extendable to two years. The successful candidate will work on the development and application of new algorithms for the calculation of electronic properties of materials within the framework of Density Functional Theory. The goal of the first year of the project is the implementation of a method based on linear response for the efficient and accurate computational prediction of NMR spectra of realistically large model systems, with special attention to bio-systems.

Applicants should have or be about to obtain a PhD in physics, material science, chemistry or in related fields. A good experience in computer modeling and in electronic structure calculations are highly preferred. Interest in algorithmic/mathematical development and scientific programming ability, including parallel programming, are desired.

Candidates should send a resume including an outline of their research achievements as well as information for academic reference to

Juerg Hutter,
Universität Zürich,
Physikalisch Chemisches Institut,
Winterthurerstrasse 190,
CH-8057 Zürich

E-Mail: hutter@pci.unizh.ch
Phone: +41 1 635 44 91 Fax: +41 1 635 68 38

POSTDOCTORAL RESEARCHER

LAWRENCE LIVERMORE NATIONAL LABORATORY, CALIFORNIA

Applicants are invited for postdoctoral research in the area of quantum simulations of nanostructures, fluids and solids under extreme condition in the Quantum Simulations Group (QSG) at the Lawrence Livermore National Laboratory (LLNL), California, USA.

The requirements for this position include a PhD in Physics, Chemistry or Materials Science and preferably some experience in electronic structure calculations and quantum simulations, e.g. ab-initio molecular dynamics and quantum Monte Carlo techniques.

Please submit your CV, publications list, and three letters of recommendation to:

Dr. Giulia Galli, LLNL, P. O. Box 808, L-415, Livermore, CA 94550.

The deadline for applications is January 1, 2005 or until the position is filled.

LLNL/QSG information can be found at: http://www.llnl.gov/ and

http://www-pat.llnl.gov/Research/qsg/

Lawrence Livermore National Laboratory is an Affirmative Action/Equal Opportunity Employer.

PROFESSOR POSITIONS IN COMPUTATIONAL BIOSCIENCES

CENTER FOR COMPUTATIONAL SCIENCES, UNIVERSITY OF TSUKUBA

Applications are invited for two faculty positions in computational biosciences at Center for Computational Sciences (CCS) in University of Tsukuba, Japan. The rank of the two positions is that of full professor but a lower rank of associate professor may be considered for younger candidates. CCS formerly known as Center for Computational Physics has been expanded in April of 2004, launching the field of computational nano- and bio-sciences by establishing the Division of Materials and Life Sciences with 11 faculty positions. CCS seeks individuals of the highest international caliber who lead the research activity in computational biosciences at CCS on appointment. The successful applicant is expected to have a strong background and excellent research activities in computational bioscience and/or computational molecular and condensed-matter sciences. The applicant is expected to teach at both Graduate School of Pure and Applied Sciences and College of Natural Sciences in University of Tsukuba. However, the teaching duty is relatively light in comparison with standards of faculty positions at other national universities in Japan. Computational facilities at CCS are excellent: CCS and University of Tsukuba own the state-of-the- art massively parallel computers and vector-parallel super- computers, respectively, and further replacement of these computers is planned within a few years; other supercomputers located in several places in Japan are accessible upon application of research proposals. Salary will be commensurate with qualifications and experience, being subject to the regulation of Japan government. Medical insurance and other benefits are equivalent to those of employees of Japan government.

Please send a curriculum vitae, a publication (or accomplishment) list, reprints (copies) of five most important publications, description of research experience, description of your research plan at CCS, and two letters of reference to:

Professor Akira Ukawa
Director, Center for Computational Sciences
University of Tsukuba
1-1-1 Tennodai, Tsukuba 305-8577, Japan

Application deadline is December 24, 2004.

If you have any inquiry regarding this announcement, please contact:

Professor Atsushi Oshiyama
Head, Division of Materials and Life Sciences, CCS
University of Tsukuba
Email: oshiyama@comas.frsc.tsukuba.ac.jp
Phone: +81-298-853-5908

CCS, Univesity of Tsukuba: http://www.ccs.tsukuba.ac.jp/index.html

Postdoctoral position and **Research associate** position

in NREL's Solid State Theory Group in: **Theory of Magnetic Semiconductors** and **Theory of Nanostructures**

National Renewable Energy Laboratory (NREL)
`http://www.sst.nrel.gov`

NREL's Solid State Theory Group is looking to fill two temporary positions: a Postdoctoral position and a Research Associate position . The research areas include Electronic Structure Theory of Semiconductor Nanostructures, magnetic semiconductors (spintronics), and development of advanced theoretical methods for electronic structure calculations. The positions are for up to 3 years. The salary range is $45,000- $62,000 per year, depending on seniority, qualification and experience. Applicants are expected to have a strong background in solid-state theory. The positions are with Alex Zunger, Solid State Theory Group Leader. The start date is between January 2005 and summer 2005. Applications for both positions are being considered now. For more details about ongoing work, see `http://www.sst.nrel.gov`.

The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists. The group has outstanding computational facilities, 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, current and past personnel and facilities.

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

Alex Zunger, M/S 3213
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401

Clarification or further details can be obtained via email to `alex_zunger@nrel.gov`

NREL is an equal opportunity employer and proud of its commitment to diversity. Women and minorities are encouraged to apply.

POSTDOCTORAL POSITIONS IN THEORETICAL/COMPUTATIONAL CHEMISTRY/PHYSICS

Department of Chemistry and Chemical Biology and Department of Physics and Astronomy, Rutgers University

One or more post-doctoral positions are available, begining as early as January or as late as September 2005, in Kieron Burke's research group (http://dft.rutgers.edu). The general research area is density functional theory (DFT) of electronic structure and response. Our research includes development of time-dependent DFT calculations of transport through single molecules and of electron-molecule scattering. A background in theory and/or computation is required. Please send vita to kieron@dft.rutgers.edu (pdf format preferred), plus 3 letters of reference.

Assoc. Prof Kieron Burke
Dept Chemistry & Chem. Biology
Rutgers University
610 Taylor Rd, Piscataway, NJ 08854
Telephone: (732)445-1785 (office),-2618 (dept),-5312 (Fax)
E-mail: kieron@dft.rutgers.edu
Fall 04: Mon+Weds Princeton Materials Inst. (609)258-7480

Research Associate: Developing Multiscale Techniques to Connect the Quantum to the Mesoscopic Level

Theoretical Chemistry, Ruhr-Universitaet Bochum, Germany

Applications are invited for a research associate position. Subject to funding the preferred starting date would be in 2004 or early 2005.

The ideal candiate would have significant experience in electronic structure theory, mixed quantum/classical simulation, and dynamical multiscale simulation. She or he would work primarily on developing and implementing novel techniques to connect a quantum description (Car-Parrinello) via a microscopic level to a coarse-grain treatment. Although the ultimate goal is to predict properties of soft materials under irradiation, the project focuses heavily on code development in close collaboration with an outstanding partner group. In addition, he/she can also be involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center of Theoretical Chemistry at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references to office@theochem.rub.de (one pdf file preferred).

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

`Professor Dominik Marx`
`Lehrstuhl fuer Theoretische Chemie`
`Ruhr-Universitaet Bochum`
`44780 Bochum, Germany`
`Email: office@theochem.rub.de`
`Fax: ++49 234 32 14045`
`URL: http://www.theochem.rub.de/`

PhD Studentship: Materials Science and Nanotechnology
Theoretical Chemistry, Ruhr-Universitaet Bochum, Germany

Applications are invited for a PhD position embedded in our international doctorate study program which gives individual support to our foreign graduate students. The preferred starting date would be spring 2005.

You will learn about state–of–the–art electronic structure and ab initio simulation techniques and apply them to challenging problems at the nanoscale in order to understand complex materials and processes. Candiates should have, or be about to receive, an honors degree in Physics or Chemistry with a solid background in theory.

Information on the techniques used and developed are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Theoretical Chemistry Center at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their achievements and interests as well as contact information for academic references, preferrentially one file, to office@theochem.rub.de.

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
Fax: ++49 234 32 14045
URL: http://www.theochem.rub.de/

Lecturer in Theoretical Chemistry
Department of Chemistry, University of Cambridge, U.K.

The Department of Chemistry in Cambridge will be appointing a Lecturer in Theoretical Chemistry to take office on October 1st 2005 or shortly thereafter. The closing date for applications is December 17th 2004.

Details can be found on

http://www.jobs.ac.uk/jobfiles/BI899.html

Sue Harding
p.p. Michiel Sprik

Faculty Position in Condensed Matter Theoretical Physics
Department of Physics, University of California, Davis

The Department of Physics at the University of California at Davis invites applications for a faculty position in theoretical condensed matter physics. The appointment will be at the tenure-track Assistant or tenured Associate Professor level as determined by qualifications and experience. The targeted starting date for appointment is July 1, 2005. The successful candidate will join our sixteen member condensed matter physics group, and will have the opportunity to become involved in the campus Center for Computational Science and Engineering. Our Department is looking to further broaden and strengthen our expertise in the areas of density functional theory, strongly correlated electron systems, large scale first principles molecular dynamics simulations, or related areas involving electronic and magnetic behavior of condensed systems.

The existing condensed matter group consists of seven theorists and nine experimentalists. Principal activities include both experimental and theoretical studies of: magnetic, superconducting and strongly correlated materials, including high temperature superconductivity and spintronic phenomena; surface dynamics, microscopy (STM, LEEM), and spectroscopy and holography using synchrotron sources; nanomaterials and nanotechnology; disordered systems; and low temperature magnetism and quantum fluids. For more information see

http://sexton.ucdavis.edu/CondMatt/

The successful candidate will have a PhD in physics or the equivalent and be expected to teach at the undergraduate and graduate levels. The position is open until filled, but to assure full consideration, applications should be received no later than January 21, 2005. To initiate the application process, please mail your curriculum vitae, publication list, research statement, and the names (including address, e-mail, fax, and phone number) of three or more references to:

Professor Shirley Chiang, Chair
Department of Physics
University of California, Davis
One Shields Avenue
Davis, CA 95616-8677

Further information about the department may be found on our website at

http://www.physics.ucdavis.edu.

The University of California is an affirmative action/equal opportunity employer.

Post-doctoral and PhD positions in "Electronic excitations at surfaces"

The International University Bremen, Germany

Positions for a post-doctoral fellow or for PhD candidates are available at the International University Bremen, in the "Theory of Condensed Matter" group headed by Prof. Dr. Michael Rohlfing.

The prospective candidates will mainly work on electronic properties of clean and adsorbate-covered surfaces, focusing on excited electronic states, their spectra, and related short-time dynamics (desorption processes and femtosecond charge-carrier dynamics). Possible topics include spectra of PTCDA on metal substrates, laser-induced desorption from insulator surfaces, and excitation-induced dynamics of silicon surfaces. Density functional theory and ab-initio many-body perturbation theory (GW method and Bethe-Salpeter equation techniques) will be employed. A solid background in computational solid-state physics or computational chemistry and programming skills in FORTRAN or C will be considered favourably.

International University Bremen (in Bremen, Germany) is a newly founded private university aiming at high-level research and teaching in an international environment. With English as our working language and more than 70 nations on campus, IUB provides excellent research and working conditions and a unique intercultural atmosphere.

The positions are for two years (three to four years for the PhD positions). The salary corresponds to the BAT IIa level (1/2 BAT IIa for the PhD candidates) common at German public universities.

For further information, visit our website at

http://imperia.iu-bremen.de/ses/physics .

The positions are immediately available and applications will be considered until the positions are filled. Further requests and applications (including a CV, names and addresses of three references, summary of research interests, and list of publications) should be directed to Prof. Dr. Michael Rohlfing (m.rohlfing@iu-bremen.de).

Prof. Dr. Michael Rohlfing
School of Engineering and Science
International University Bremen
P.O. Box 750 561
D-28725 Bremen
Germany

Phone: +49 421 200-3222,
Fax: +49 421 200-3229,

Mobile: +49 160 99793368
Office: Research III, Room 49,
Campus Ring 1,
28759 Bremen, Germany

E-mail: m.rohlfing@iu-bremen.de
Info: http://imperia.iu-bremen.de/ses/physics

Postdoctoral Research Associates (3 positions) in Computational Materials Chemistry

Nanochemistry Research Institute at Curtin University, Perth, Australia

Three postdoctoral positions exist within the Computational Chemistry Group of the Nanochemistry Research Institute at Curtin University to work in the area of development and application of theoretical methods to materials chemistry. The areas of research for the positions include:

(1) Developments to the SIESTA program for linear-scaling quantum mechanics, including new functionality and improved parallelism.

(2) Combined use of ab initio methods and kinetic Monte Carlo for the study of fuel cell materials.

(3) Computational materials chemistry, including materials for energy storage, phase transformations and catalysis.

The work will exploit parallel computing using both in-house facilities, as well as the new supercomputers being procured for both State (IVEC) and Federal (APAC) facilities.

Any interested candidates should send a CV, with the names of at least 2 referees, to Prof. Julian Gale who will also be happy to provide further details.

Location: Nanochemistry Research Institute, Curtin University of Technology, Perth, Western Australia.

Qualifications: Candidates should possess a PhD and a background in either theoretical chemistry or physics, preferably with experience of condensed phase techniques. Experience of programming in f90 and MPI is desirable.

Duration: 2 to 4 years, depending on position, commencing early 2005.

Prof Julian D. Gale
Premier's Research Fellow/Professor of Computational Chemistry,
Nanochemistry Research Institute,
Department of Applied Chemistry,
Curtin University of Technology,
P.O. Box U1987,
Perth 6845,
Western Australia
Ph : +61 8 9266 7172
Fax: + 61 8 9266 4699

Email : julian@power.curtin.edu.au
http://nanochemistry.curtin.edu.au/people/julian.cfm
http://gulp.curtin.edu.au/

Ph.D position in Condensed Matter Theory

Tyndall National Institute/National Microelectronics Research Centr

University College Cork, Cork, Ireland

We have an opening for a Ph.D student in the Computational Modelling group of the Tyndall National Institute. The Tyndall Institute is Ireland's national research institute for Information and Communication Technologies and includes the NMRC (http://www.nmrc.ie) as well as research groups from University College Cork (http://www.ucc.ie), and Science Foundation Ireland

(http://www.sfi.ie).

The position involves understanding and simulating computationally electron transport through single molecules (molecular electronics), with a focus on treating the quantum electron-electron interaction accurately. The technological application is to understand the physics of the smallest possible transistors, of dimensions of a few nanometers.

For general information on the Computational Modelling Group, please view www.nmrc.ie/research/computat
modelling-group

To apply, send a CV including the names of two referees to Dr Paul Delaney, paul.delaney@nmrc.ie

Postdoctoral Position

LDA+DMFT/Order-N Research Project (JST-CREST)

University of Tokyo/National Institute of Advanced Industrial and Technology

JST Postdoctoral Research Associate

Three new postdoctoral research positions are open for CREST-JST 5-year-program involving LDA/GW+DMFT and Large Scale Electronic Structure Theory. The program involves a team of investigators at Department of Applied Physics, University of Tokyo in Tokyo and at Research Institute for Computational Science (RICS), National Institute of Advanced Industrial and Technology (AIST) in Tsukuba. The possible candidates are expected to have specific experience with first-principles methods and computational materials science. Two of them should work in LDA/GW+DMFT, associated with T.Fujiwara (U.Tokyo, Tokyo) and F.Aryasetiawan (AIST, Tsukuba), and one in Order-N method with T.Fujiwara.

Initial appointment, starting from April 2005, will be for one year. Successful candidates can extend the appointment for 4 years. To apply, please send, not later than the end of January 2005, Curriculum Vita, List of publications and two letters of recommendation, by ordinary mail or e-mail to:

Professor Takeo Fujiwara, Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan. (fujiwara@coral.t.u-tokyo.ac.jp)

Clarifications or further details can be obtained via e-mail to

(fujiwara@coral.t.u-tokyo.ac.jp) or (f-aryasetiawan@aist.go.jp).

7 Abstracts

Hysteresis effect in FePd magnetic stripes studied by coherent soft x-ray resonant magnetic scattering

K. Chesnel
DRFMC, CEA-Grenoble, 17 avenue des Martyrs, 38054 Grenoble, France
ALS, Lawrence Berkeley National Laboratory, CA 94720, USA
G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
F. Livet
LTPCM, ENSEEG-Domaine Universitaire, Saint-Martin d'Hères, France
G. Beutier, A. Marty and M. Belakhovsky
DRFMC, CEA-Grenoble, 17 avenue des Martyrs, 38054 Grenoble, France
A. Haznar
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
Inst. of Low Temp. and Struc. Res. Polish Acad. Sci., PO Box 1410, Wroclaw, Poland
S. P. Collins
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
Diamond Light Source, Rutherford Appleton Laboratory, Didcot OX11 0QX, UK

Abstract

An FePd thin film sample, showing magnetic stripe domains as imaged by magnetic force microscopy, has been measured by soft x-ray resonant magnetic scattering in reflection geometry. Illumination with coherent radiation, produced by inserting a 20 μm pinhole in front of the sample, leads to a magnetic speckle pattern in the scattered intensity that gives access to the domain morphology. Application of an in-plane magnetic field for a few seconds gives a strong change in the observed intensity fluctuations, which indicates a large degree of variation between the two patterns taken before and after field exposure. ¿From the speckle pattern we calculate a degree of coherence of $\beta = 0.5$ for the incident beam.

Accepted for publication in J. Synchrotron Rad. **11**, 469–475 (2004)
Manuscript available from g.van_der_laan@dl.ac.uk
See also journal cover illustration, at

http://journals.iucr.org/s/issues/2004/06/00/issconts.html

Electronic structure of transition metal impurities in p-type ZnO

L. Petit[1], T. C. Schulthess[1], A. Svane[2], Z. Szotek[3], W.M. Temmerman[3],
and A. Janotti[1]
[1] *Computer Science and Mathematics Division,*
and Center for Computational Sciences
Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[2] *Institute of Physics and Astronomy, University of Aarhus,*
DK-8000 Aarhus C, Denmark
[3] *Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

The self-interaction corrected local spin-density approximation is used to investigate the ground-state valency configuration of transition metal (TM=Mn, Co) impurities in p-type ZnO. Based on the total energy considerations, we find a stable localised TM^{2+} configuration for a TM impurity in ZnO if no additional hole donors are present. Our calculations indicate that the (+/0) donor level is situated in the band gap, as a consequence of which the TM^{3+} becomes more favourable in p-type ZnO, where the Fermi level is positioned at the top of the valence band. When co-doping with N, it emerges that the carrier-mediated ferromagnetism can be realized in the scenario where the N concentration exceeds the TM impurity concentration. If TM and N concentrations are equal, the shallow acceptor levels introduced by N are fully compensated by delocalised TM d-electrons.

(Submitted to Phys. Rev. Lett., cond-mat/0410628)
Contact person: petitl@ornl.gov

Spin polarization and barrier-oxidation effects at the Co/alumina interface in magnetic tunnel junctions

N. D. Telling and G. van der Laan
Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK
S. Ladak and R. J. Hicken
School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK

Abstract

The electronic structure and polarization in magnetic tunnel junctions prepared with varying degrees of barrier-layer oxidation have been studied using x-ray absorption spectroscopy across the Co $L_{2,3}$ absorption edges. It was found that the Co electronic structure near the Co/alumina interface tended to that of cobalt oxide as the barrier oxidation time was increased. However, the net Co 3*d* spin polarization, determined from x-ray magnetic circular dichroism, increased for moderate oxidation times compared to that obtained for an under-oxidized Co/Al interface. It is proposed that the expected dilution of the measured polarization due to the formation of (room temperature) paramagnetic cobalt oxide, is offset by an increase in the Co 3*d* spin-polarization of the interface layer as the interface bonding changes from Co-Al to Co-O with increasing oxidation times.

Accepted for publication in Appl. Phys. Lett. **85**, 3803 - 3805 (2004).
Manuscript available from g.van_der_laan@dl.ac.uk

Hyperfine interactions
at lanthanide impurities in Fe

D. Torumba, S. Cottenier, V. Vanhoof, M. Rots
K.U.Leuven, Instituut voor Kern- en Stralingsfyscia,
Celestijnenlaan 200 D, B-3001 Leuven

Abstract

The magnetic hyperfine field and electric-field gradient at isolated lanthanide impurities in an Fe host lattice are calculated from first principles, allowing for the first time a qualitative and quantitative understanding of an experimental data set collected over the past 40 years. It is demonstrated that the common Local Density Approximation leads to quantitatively and qualitatively wrong results, while the LDA+U method performs much better. In order to avoid pitfalls inherent to the LDA+U method, a careful strategy had to be used, which will be described in detail. The lanthanide 4f spin moment couples antiferromagnetically to the magnetization of the Fe lattice, in agreement with the model of Campbell and Brooks. There is strong evidence for a delocalization-localization transition that is shifted from Ce to at least Pr. This shift is interpreted in terms of the effective pressure felt by lanthanides in Fe. For the localized lanthanides, Yb is shown to be divalent in this host lattice, while all others are trivalent (including Eu, the case of Tm is undecided). The completely filled and well-bound 5p shell of the lanthanides is shown to have a major and unexpected influence on the dipolar hyperfine field and on the electric-field gradient, a feature that can be explained by their $1/r^3$ dependence. An extrapolation to actinides suggests that the same is true for the actinide 6p shell. The case of free lanthanide atoms is discussed as well.

Submitted to: Physical Review B
Pdf-file available from Stefaan.Cottenier@fys.kuleuven.ac.be

Effects of short-range order on the electronic structure of disordered metallic systems

D. A. Rowlands
H.H. Wills Physics Laboratory, University of Bristol,
Bristol BS8 1TL, U.K.
J. B. Staunton
Dept. of Physics, University of Warwick, Coventry CV4 7AL, U.K.
B. L. Györffy
H.H. Wills Physics Laboratory, University of Bristol,
Bristol BS8 1TL, U.K.
E. Bruno, B. Ginatempo
Dipartimento di Fisica, Universita di Messina,
Salita Sperone 31, 98166 Messina, Italy

Abstract

For many years the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA) has been widely used to describe the electronic structure of disordered systems based upon a first-principles description of the crystal potential. However, as a single-site theory the KKR-CPA is unable to account for important environmental effects such as short-range order (SRO) in alloys and spin fluctuations in magnets, amongst others. Using the recently devised KKR-NLCPA (where NL stands for nonlocal), we show how to remedy this by presenting explicit calculations for the effects of SRO on the electronic structure of the *bcc* $Cu_{50}Zn_{50}$ solid solution.

(Submitted to Phys. Rev. Lett.)
A preprint is available on cond-mat/0411347

Contact person: d.a.rowlands@bristol.ac.uk

Tracking the Local Reversal Processes in Nanostructures by Magnetic Speckles

Karine Chesnel
ALS, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
DRFMC, CEA-Grenoble, 17 avenue des Martyrs, 38054 Grenoble, France
Michel Belakhovsky
DRFMC, CEA-Grenoble, 17 avenue des Martyrs, 38054 Grenoble, France
Gerrit van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington, WA4 4AD, UK
Frederic Livet
LTPCM, ENSEEG-Domaine Universitaire, Saint-Martin d'Hères, France
Alain Marty and Guillaume Beutier
DRFMC, CEA-Grenoble, 17 avenue des Martyrs, 38054 Grenoble, France
Stephen P. Collins
Diamond Light Source, Rutherford Appleton Laboratory, Didcot, UK
Annaa Haznar
Magnetic Spectroscopy, Daresbury Laboratory, Warrington, WA4 4AD, UK
ILT&SR, Polish Acad. Sci., PO Box 1410, 50-950 Wroclaw 2, Poland

Abstract

We have used coherent soft x-ray resonant magnetic scattering to locally track reversal processes in magnetic nanostructures. Coherent illumination of a limited number of nano-objects in a CoPt nanoline grating produces a specific speckle pattern, whose evolution under *in situ* magnetic field reveals the true local magnetic ordering. While each nanoline behaves as a single macrospin whose direction depends on the dipolar coupling with neighbors, the global reversal of the line array is successively governed by two effects, first by the random distribution of defects, followed by the dipolar coupling favoring antiferromagnetic ordering.

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Reprints available from g.van_der_laan@dl.ac.uk

Active sites for the vapor phase Beckmann rearrangement over mordenite: An ab initio study

T. Bucko, J. Hafner and L. Benco
Institut für Materialphysik and Center for Computational Material Science, Universität Wien, Sensengasse, A-1090 Wien, Austria

Abstract

The reaction mechanisms of the Beckmann rearrangement (BR) of cyclohexanone oxime to ϵ-caprolactam in the gas phase and catalyzed by mordenite are investigated. For the gas phase reaction, starting with the protonated oxime, the rate-controlling step is the transformation of the N-protonated to an O-protonated species (1,2-H-shift) with an activation energy of 178 kJ/mol. The barriers for the subsequent reaction steps of the transformation to N-protonated ϵ-caprolactam are significantly lower, 10 kJ/mol and 54 kJ/mol N-insertion and hydrolysis of the carbiminium ion. As possible active sites in the zeolite, Brønsted acid (BA) sites, silanol nests, and surface silanol groups are considered. The most favorable reaction path comprising three reaction barriers of 88 kJ/mol, 64 kJ/mol and 40 kJ/mol for the 1,2-H transfer, the N-insertion and the hydrolysis of the carbiminium ion has been found for a BA site. H-bonding is found to play a key role in the reaction catalyzed by weak acid sites. The activation energies for the rate-controlling step of the Beckmann rearrangement increases in order BA site (142 kJ/mol - 1,2-H-shift+N-insertion) < silanol nest (184 kJ/mol - 1,2-H-shift+N-insertion) < H-bonded terminal silanol groups (223 kJ/mol - N-insertion) < isolated silanol group (266 kJ/mol - N-insertion). We have also used harmonic transition state theory to calculate the reaction rates for catalysis by BA sites and silanol nest. Due to the large difference in the activation energies of the individual steps, the BR catalyzed by BA sites or silanol nests behave like simple first-order reactions with effective reaction barriers of 142 kJ/mol and 184 kJ/mol, respectively. The reaction at BA sites is about five orders of magnitude faster than that at a silanol nest. However, the actual turn-over of a reaction catalyzed by BA sites might by slowed down by the relatively high desorption energy of the product, and frequent readsorption and desorption at an increased concentration of BA sites.

(Accepted, J. Chem. Phys. B)

Contact person: tomas.bucko@univie.ac.at

CO adsorption on the Pt(111) surface: a comparison of a gradient corrected functional and a hybrid functional

K. Doll
Institut für Mathematische Physik, TU Braunschweig,
Mendelssohnstrasse 3, D-38106 Braunschweig

Abstract

The adsorption of CO on the Pt(111) surface in a $(\sqrt{3} \times \sqrt{3})$ pattern has been studied with the gradient corrected functional of Perdew and Wang and the B3LYP hybrid functional. A slab which is periodic in two dimensions is used to model the system. The Perdew-Wang functional incorrectly gives the fcc site as the most favorable adsorption site, in accord with a set of previous studies. The B3LYP functional gives the top site as the preferred site. This confirms results from cluster studies where it was suggested that the different splitting, dependent on the functional, between highest occupied and lowest unoccupied molecular orbital, could be the reason for this change of the adsorption site. This is supported by an analysis based on the projected density of states and the Mulliken population.

(Submitted to: Surface Science)
Contact person: k.doll@tu-bs.de

Ab initio study of transition-metal silicide films on Si(001)

Hua Wu, Peter Kratzer, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin-Dahlem, Germany

Abstract

Density-functional theory calculations are used to identify trends both of thermodynamic stability and magnetism in the pseudomorphic CsCl-like SiM (M=Mn,Fe,Co,Ni) thin films on Si(001). The results, which can be accounted for in terms both of the energy separation between Si $3s3p$ and M $3d$ valence bands and of the M $3d$ orbital occupation, are helpful to understand experimental findings. It is implied that the ultrathin SiMn film may be a magnetoelectronic material.

(submitted to: Proc. 27th Int. Conf. on the Physics of Semiconductors)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

Nanometer and sub-nanometer thin oxide films at surfaces of late transition metals

Karsten Reuter
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin-Dahlem (Germany)

Abstract

If metal surfaces are exposed to sufficiently oxygen-rich environments, oxides start to form. Important steps in this process are the dissociative adsorption of oxygen at the surface, the incorporation of O atoms into the surface, the formation of a thin oxidic overlayer and the growth of the once formed oxide film. For the oxidation process of late transition metals (TM), recent experimental and theoretical studies provided a quite intriguing atomic-scale insight: The formed initial oxidic overlayers are not merely few atomic-layer thin versions of the known bulk oxides, but can exhibit structural and electronic properties that are quite distinct to the surfaces of both the corresponding bulk metals and bulk oxides. If such nanometer or even sub-nanometer surface oxide films are stabilized in applications, new functionalities not scalable from the known bulk materials could correspondingly arise. This can be particularly important for oxidation catalysis, where technologically relevant gas phase conditions are typically quite oxygen-rich. In such environments surface oxides may even form naturally in the induction period, and actuate then the reactive steady-state behavior that has traditionally been ascribed to the metal substrates. Corresponding aspects are reviewed by focusing on recent progress in the modeling and understanding of the oxidation behavior of late TMs, using particularly the late 4*d* series from Ru to Ag to discuss trends.

(to appear in: Nanocatalysis: Principles, Methods, Case Studies, U. Heiz, H. Hakkinen and U. Landman (Eds.), Springer, Berlin)

Contact person: Karsten Reuter (reuter@fhi-berlin.mpg.de)

Dissociation of O_2 at Al(111): The Role of Spin Selection Rules

Jörg Behler[1], Bernard Delley[2], Sönke Lorenz[1], Karsten Reuter[1], Matthias Scheffler[1]
[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4–6, D-14195 Berlin, Germany
[2] *Paul-Scherrer-Institut, HGA/123, CH-5232 Villigen PSI, Switzerland*

Abstract

A most basic and puzzling enigma in surface science is the description of the dissociative adsorption of O_2 at the (111) surface of Al. Already for the sticking curve alone, the disagreement between experiment and results of state-of-the-art first-principles calculations can hardly be more dramatic. In this paper we show that this is caused by hitherto unaccounted spin selection rules, which give rise to a highly non-adiabatic behavior in the O_2/Al(111) interaction. We also discuss problems caused by the insufficient accuracy of present-day exchange-correlation functionals.

(submitted to: Physical Review Letters)
Contact person: Jörg Behler (behler@fhi-berlin.mpg.de)

Structure, Energetics and Properties of $Fe_3O_4(001)$ from First Principles

R. Pentcheva and W. Moritz
Dept. of Earth and Environmental Sciences, University of Munich,
Theresienstr. 41, 80333 Munich, Germany
F. Wagner
Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften,
Barerstr. 21, 80333 Munich, Germany
M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany

Abstract

(in "High Performance Computing in Science and Engineering", Springer Verlag, p.375, 2004)
Contact person: Rossitza Pentcheva (pentcheva@lrz.uni-muenchen.de)

Describing static correlation in bond dissociation by Kohn-Sham density functional theory

M. Fuchs
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany
Y.-M. Niquet
Département de Recherche Fondamentale sur la Matière Condensée,
SP2M/L_Sim, CEA Grenoble, 38054 Grenoble Cedex 9, France
X. Gonze
Unité PCPM, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
K. Burke
Dept. of Chemistry and Chemical Biology, Rutgers University,
610 Taylor Road, Piscataway, NJ 08854, U.S.A.

Abstract

We show that density functional theory within the RPA (random phase approximation for the exchange-correlation energy) provides a correct description of bond dissociation in H_2 in a spin-restricted Kohn-Sham formalism, i.e. without artificial symmetry breaking. We present accurate adiabatic connection curves both at equilibrium and beyond the Coulson-Fisher point. The strong curvature at large bond length implies important static (left-right) correlation, justifying modern hybrid functional constructions but also demonstrating their limitations. Although exact at infinite and accurate around the equilibrium bond length, the RPA dissociation curve displays unphysical repulsion at larger but finite bond lengths. Going beyond the RPA by including the exact exchange kernel (RPA+X), we find a similar repulsion. We argue that this deficiency is due to the absence of double excitations in adiabatic linear response theory. Further analyzing the H_2 dissociation limit we show that the RPA+X is not size-consistent, in contrast to the RPA.

(submitted to: J. Chem. Phys. [19 October 2004])

Contact person: Martin Fuchs (fuchs@fhi-berlin.mpg.de)

Jahn-Teller stabilization of a "polar" metal oxide surface: $Fe_3O_4(001)$

R. Pentcheva, F. Wendler, H.L. Meyerheim, W. Moritz
Dept. of Earth and Environmental Sciences, University of Munich,
Theresienstr. 41, 80333 Munich, Germany
N. Jedrecy
Lab. Mineralogie-Cristallographie, Université Paris 6 et 7,
4 place Jussieu, F-75252 Paris, France
M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany

Abstract

Using *ab initio thermodynamics* we compile a phase diagram for the surface of $Fe_3O_4(001)$ as a function of temperature and oxygen pressures. A hitherto ignored polar termination with octahedral iron and oxygen forming a *wave-like* structure along the [110]-direction is identified as the lowest energy configuration over a broad range of oxygen gas-phase conditions. This novel geometry is confirmed in a x-ray diffraction analysis. The stabilization of the $Fe_3O_4(001)$-surface goes together with dramatic changes in the electronic and magnetic properties, *e.g.*, a halfmetal-to-metal transition.

(submitted to: Phys. Rev. Lett. (June 2004))
Contact person: Rossitza Pentcheva (pentcheva@lrz.uni-muenchen.de)

Image States in Metal Clusters

Patrick Rinke[1,3], Kris Delaney[1,4], P. García-González[2], R. W. Godby[1]
[1] *Department of Physics, University of York, Heslington,*
York YO10 5DD, United Kingdom
[2] *Departamento de Física Fundamental, U. N. E. D.*
28080 Madrid, Spain
[3] *Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4–6, D-14195 Berlin, Germany
[4] *Present address: Department of Physics, University of Illinois,*
at Urbana-Champaign, Urbana IL 61801-3080, USA

Abstract

The existence of image states in small clusters is shown, using a quantum-mechanical many-body approach. We present image state energies and wavefunctions for spherical jellium clusters up to 186 atoms, calculated in the GW approximation, which by construction contains the dynamic long-range correlation effects that give rise to image effects. In addition we find that image states are also subject to quantum confinement. To extrapolate our investigations to clusters in the mesoscopic size range we propose a semi-classical model potential, which we test against our full GW results.

(accepted by: Physical Review A)
Contact person: Patrick Rinke (rinke@fhi-berlin.mpg.de)

Ab initio Study of Microscopic Processes in the Growth of Co on Cu(001)

R. Pentcheva
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany

Abstract

Using density-functional theory we investigate the energetics of various diffusion processes relevant for the heteroepitaxial growth of Co on Cu(001). We focus on how the barrier height depends on the local coordination, the interaction with the substrate and spin-polarization. We determine the temperature at which the different atomistic processes are activated and discuss their implications for the growth morphology. In particular, atomic exchange divides the temperature scale into two distinct regions: At lower temperatures growth proceeds similar to the homoepitaxial case, above the activation temperature of exchange a qualitatively different bimodal surface morphology evolves.

(accepted for publication: Appl. Phys. A)
Contact person: Rossitza Pentcheva (pentcheva@lrz.uni-muenchen.de)

Structural phase transition of boron nitride compound

Y. Al-Douri
Department of Physics, Faculty of Science, National University of Singapore,
Singapore 119260

Abstract

The full-potential band-structure scheme based on the linear combination of overlapping nonorthogonal local-orbital (FPLO) is used. The crystal potential and density are represented as a lattice sum of local overlapping nonspherical contributions. The energetic transitions of BN of zinc-blende and wurtzite structures are calculated using the band structure scheme. The energy gap at ambient pressure is found to be indirect for the two structures. The structural properties of two structures of BN are (obtained from the total energy calculations) and the total density of states are calculated. The phase transition parameter of BN is investigated. The ionicity character of BN has been calculated to test the validity of our recent models. The results are in reasonable agreement with experimental and other theoretical results.

(Solid State Communications 132 (2004) 465-470)
Contact person: yaldouri@yahoo.com

Towards half-metallic interfaces: the Co_2CrAl/InP contacts

I. Galanakis

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

Although the interest on half-metallic Heusler alloys, susceptible to be used in spintronic applications, has considerably grown, their interfaces with semiconductors show very low spin-polarization. I identify mechanisms which can keep the high spin-polarization at the interface (more than 80% of the electrons at the Fermi level are of majority spin) although the half-metallicity is lost. The large enhancement of the Cr moment at the interface between a CrAl terminated $Co_2CrAl(001)$ spacer and the InP(001) semiconductor weakens the effect of the interface states resulting in this high spin-polarization. On the other hand the Co_2CrAl/InP interfaces made up by a Co layer and either an In or a P one show a severe decrease of the Co spin moment but Cr in the subinterface layer is bulklike and the resulting spin-polarization is similar to the CrAl-based interfaces.

Journal of Physics: Condensed Matter **16**, 8007 (2004)
Reprint available from: I.Galanakis@fz-juelich.de

Influence of spin-orbit coupling on the band gap of Heusler alloys

Ph. Mavropoulos[1], I. Galanakis[1], V. Popescu[2],
and P.H. Dederichs[1]

[1] *Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*

[2] *Department Chemie/Physikalische Chemie, University of Munich, Butenandtstr. 5-13, D-81377 Munich, Germany*

Abstract

The band gap of half-metallic ferromagnets can be affected by the spin-orbit coupling, which introduces there a small, but non-vanishing, density of states. We study this effect in the case of Heusler alloys. We find that, as a rule, the spin polarisation in the middle of the gap decreases for compounds of heavier elements.

Journal of Physics: Condensed Matter **16**, S5759 (2004)
Reprint available from: Ph.Mavropoulos@fz-juelich.de

Electronic and magnetic properties of the (111) surfaces of NiMnSb

I. Galanakis
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

Using an ab-initio electronic structure method, I study the (111) surfaces of the half-metallic NiMnSb alloy. In all cases there is a very pronounced surface state within the minority gap which destroys the half-metallicity This state survives for several atomic layers below the surface contrary to the (001) surfaces where surface states were located only at the surface layer. The lower dimensionality of the surface leads in general to large enhancements of the surface spin moments.

(Journal of Magnetism and Magnetic Materials, in press)
Preprint available from: arXiv:cond-mat/0408131 or I.Galanakis@fz-juelich.de

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Orbital magnetism in the half-metallic Heusler alloys

I. Galanakis
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

Using the fully-relativistic screened Korringa-Kohn-Rostoker method I study the orbital magnetism in the half-metallic Heusler alloys. Orbital moments are almost completely quenched and they are negligible with respect to the spin moments. The change in the atomic-resolved orbital moments can be easily explained in terms of the spin-orbit strength and hybridization effects. Finally I discuss the orbital and spin moments derived from X-ray magnetic circular dichroism experiments.

(Physical Review B, in press)
Preprint available from: arXiv:cond-mat/0407560 or I.Galanakis@fz-juelich.de

Interface properties of the NiMnSb/InP and NiMnSb/GaAs contacts

I. Galanakis, M. Ležaić, G. Bihlmayer, and S. Blügel
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

We study the electronic and magnetic properties of the interfaces between the half-metallic Heusler alloy NiMnSb and the binary semiconductors InP and GaAs using two different state-of-the-art full-potential *ab-initio* electronic structure methods. Although in the case of most NiMnSb/InP(001) contacts the half-metallicity is lost, it is possible to keep a high degree of spin-polarization when the interface is made up by Ni and P layers. In the case of the GaAs semiconductor the larger hybridization between the Ni-d and As-p orbitals with respect to the hybridization between the Ni-d and P-p orbitals destroys this polarization. The (111) interfaces present strong interface states but also in this case there are few interfaces presenting a high spin-polarization at the Fermi level which can reach values up to 74%.

(submitted to: Physical Review B)
Preprint available from: arXiv:cond-mat/0409333 or I.Galanakis@fz-juelich.de

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Size effects and conductivity of ultrathin Cu films

D.V. Fedorov
Physical-Technical Institute, Ural Branch of Russian Academy of Sciences,
426001 Izhevsk, Russia
P. Zahn, I. Mertig
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik,
Fachgruppe Theoretische Physik, D-06099 Halle, Germany

Abstract

We propose a model for the description of the transport properties of metallic films on a large scale of slab thickness. This model is based on solving the linearized Boltzmann equation in the relaxation-time approximation using *ab initio* calculations within the framework of the density functional theory. The expression for the relaxation time is derived from the microscopic treatment of the scattering processes and provides the correct thickness dependence for very thin as well as very thick films. The method is applied to the calculation of the in-plane conductivity and the Drude-type plasma frequency of thin Cu(001) films in the thickness range between 1 and 32 monolayers.

(Accepted, Thin Solid Films)
Contact person: zahn@physik.uni-halle.de

8 Presenting Other Programmes/Initiatives

We are organizing a long term program

Bridging Time and Length Scales in Materials Science and Bio-Physics

at the

Institute for Pure an Applied Mathematics (IPAM) in Los Angeles

http://www.ipam.ucla.edu/programs/ma2005/

This includes several workshops, for example a DFT hands-on computer course from October 30 to November 5, 2005

http://www.ipam.ucla.edu/programs/maws3/

If you (or one of your students) is interested to attend, please go to the web site and apply. We are able to give financial support to qualified Ph.D. students, postdocs, and visiting professors.

PLEASE ALSO PRINT THE POSTER

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AND PUT IT AT THE BOARDS OF YOUR INSTITUTE.

With best wishes – the organizers:

Russel Caflisch (UCLA, Mathematics and Materials Science)
Cecilia Clementi (Rice University)
Weinan E (Princeton University, Mathematics)
Michael Klein (University of Pennsylvania, Chemistry)
Christian Ratsch (UCLA, Mathematics)
Karsten Reuter (Fritz-Haber-Institute, Theory Department)
Matthias Scheffler (Fritz-Haber-Institute, Theory Department)
Klaus Schulten (University of Illinois, Physics and Biophysics)
Annabella Selloni (Princeton University)

9 SCIENTIFIC HIGHLIGHT OF THE MONTH

Learn on the fly": a multiscale hybrid simulation method for material systems

Gábor Csányi[1], T. Albaret[2], M. C. Payne[1], A. De Vita[3,4]

[1] *Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom*

[2] *Laboratoire de Physique de la Matiere Condensee et Nanostructures, Bat. Leon Brillouin, Campus de la Doua, Universite Claude Bernard Lyon 1, 43 Bld du 11 novembre 1918, 69622 Villeurbanne Cedex*

[3] *Physics Department, King's College London, Strand, London WC2R 2LS, United Kingdom*

[4] *INFM–DEMOCRITOS National Simulation Center and Center of Excellence for Nanostructured Materials (CENMAT), University of Trieste, Italy*

Abstract

We present an overview of a recently introduced hybrid molecular dynamics simulation scheme that links arbitrary atomistic techniques together in a truly seamless manner. Rather than constructing a new hybrid Hamiltonian that combines different models, we use a unique short–range classical potential and continuously tune its parameters to reproduce the atomic trajectories at the prescribed level of accuracy throughout the system.

This article is an extract from a Topical Review submission to Journal of Physics: Condensed Matter

1 Introduction

Natural phenomena occur on a variety of lengthscales, which not only roughly define scientific disciplines (physics and chemistry for the very small, biology for intermediate, geology for very long times and large lengthscales, and cosmology for the largest), but also delineate subfields within a given discipline, due to the very different experimental methods and theoretical models that are applicable at each scale. These form a multiscale hierarchy, in which parameters of larger scale models are measured or calculated on a smaller scale[1].

Yet in a large class of problems, the lengthscales cannot be separated in this way, the coupling between them is strong, and "bidirectional". This often happens when the microscopic phenomena are driven by some macroscopic force, so there is a complete feedback loop. Stress induced defect processes in solids are a good example, and brittle fracture is the prototypical problem.

In molecular biology, catalysis is often controlled by large–scale motion of macromolecules. If we wish to simulate these processes, we have to do that on more than one lengthscale *simultaneously.* Crucially, one cannot use the smallest–scale model to simulate the entire system, because it would be too expensive and hugely wasteful. A typical quantum mechanical molecular dynamics simulation can deal with hundreds of atoms, while the minimum system size that can capture the larger scale aspects can reach into hundreds of thousands of atoms. In the past decade there has been a growing effort to devise so–called *hybrid* simulation techniques, that seamlessly integrate a wide variety of different models, ranging from first principles methods to finite elements techniques, into a concurrent simulation[2, 3].

A pioneering work in this field was the *quasicontinuum method* [2], which successfully linked classical atomistic and continuum elasticity models. Here we concentrate on a lower level linkage: that of quantum mechanical to classical modelling. After mentioning general issues related to hybrid atomistic modelling, we discuss our scheme which was proposed in [4]. Finally, we present several validation tests and an example application to the brittle fracture in silicon.

2 Hybrid schemes

The objective is the following: given a large atomic system, some (perhaps small) regions of it need to be simulated with model A (which we take to be quantum mechanical), and the rest with model B (which we take to be classical atomistic). The major issues that have to be addressed are as follows.

- **Handshaking** The two models need to interact at the border that separates the two regions. If, as is natural, the system is partitioned by atoms into the regions A and B, how do each of the models react to having an artificial surface where we switch to using the other model?
- **Selection** How do we select which regions are to be treated by which model? In some cases, this might be straightforward, e.g. if we are investigating an impurity or a stationary defect. But in general, the region of interest where inherently quantum mechanical processes take place can appear, disappear and move, and we need to be able to track that.
- **Validation** Given any particular hybrid scheme, it has to be validated against fully accurate quantum mechanical calculations. A successful scheme will be insensitive to the precise location of the border between the two models, and all observables should be able to be converged by increasing the size of the quantum region.

Before we describe our scheme in detail, we have to address the question of which systems are suitable for hybrid simulation. Critically, the atomistic processes, as described by our quantum mechanical model, must be *local.* It is well known that in the vast majority of cases, quantum mechanics is local in the sense that the density matrix $\rho(\mathbf{r}, \mathbf{r}')$ is sparse, its elements decay fast as the separation between $\mathbf{r}$ and $\mathbf{r}'$ increases (this kind of locality we call *weak locality*). This is very useful for creating linear scaling electronic structure algorithms, but is not enough for a hybrid approach to be valid. What is needed is *strong locality*, which we define by

$$\frac{\partial^n}{\partial \mathbf{x}_j^n}\frac{\partial E_{\text{total}}}{\partial \mathbf{x}_i} \to 0 \quad \text{as} \quad |\mathbf{x}_i - \mathbf{x}_j| \to \infty \quad \forall\, n, i \neq j \tag{7}$$

where E_{total} is the total energy, and $\mathbf{x}_i$ and $\mathbf{x}_j$ are the atomic positions of atoms i and j. This guarantees that, if the quantum region is large enough, the trajectories that are important at the center of the quantum region are not affected by the fact that far away, the system is treated classically (and hence the microscopic trajectories will not be very accurate) and also that the trajectories in the quantum region can be computed with high accuracy by only considering a finite neighbourhood. The length scale of the decay in equation (7) thus gives a guide to how large the quantum region needs to be.

Most quantum mechanical systems either obey strong locality, or at least the parts of the Hamiltonian that do not, such as long range Coulomb forces and Van der Waals forces, can be very effectively treated purely classically, outside the hybrid framework.

3 A new scheme

We have recently proposed a novel approach to the handshaking problem[4]. While some of the analysis put forward will not be repeated here, we note that the main philosophical difference with the previous approaches is that we do not try to make a combined Hamiltonian from the separate model Hamiltonians $H_{\text{classical}}$ and H_{quantum}, rather, we focus on a purely local quantity, the force on each atom. Then, to make a seam between two models, one can compute the forces in the transition region using both models, and smoothly cross over from using one set of forces on one side of the seam to using the other set on the other side.

This can be done in a number of ways, for example, by averaging the forces, or by making the transition region large enough so that at the outer edge the two models yield practically identical forces. In practice however, we choose a third way. To see why, let us consider how the resulting forces are used in the simulation. Having given up the notion of a combined Hamiltonian, we do not have a strict conservation of the total energy anymore. What we do have, are forces on each atom at any given configuration, and thus we can perform molecular dynamics. However, doing MD directly using forces that come from a variety of different Hamiltonians is a recipe for disaster: for example, the bonds between atoms would not obey an "action–reaction" principle. So instead of varying the source Hamiltonian for the forces in space, we vary a uniformly valid Hamiltonian in time. We choose a suitably general classical Hamiltonian, and allow its parameters to be different for each atom, bond, angle etc. and also vary in time. So rather than being used directly, the above mentioned forces that are calculated using the different model Hamiltonians $H_{\text{classical}}$ and H_{quantum} are used to *tune* the parameters of our universal Hamiltonian at each time step: the parameters are varied to minimize the functional

$$\mathcal{F} = \sum \left| F_{\text{universal}} - F_{\{\text{classical, quantum}\}} \right|^2 . \tag{8}$$

The MD is then carried out using forces derived from the universal Hamiltonian. Thus the action–reaction principle is restored, and if the tuning is always successful, the resulting forces are extremely close to the separately calculated forces in each region. A very compact way to describe this scheme is that the various models that are assigned to the different parts of the system are being *instantaneously interpolated* by a universal potential. Of course, from a

practical point of view, a natural starting point for such a universal potential is an already existing well tested classical potential that gives an adequate description of near–equilibrium configurations for the system at hand.
A few comments are now in order.

- There is an alternative viewpoint from which the above scheme can be understood. Having assumed that we have a classical model that works well in most regions, let us choose this Hamiltonian as the universal one. We want to improve its accuracy in particular places in space and time and we do this by computing relevant new information in those places, using a quantum mechanical model. We then incorporate this new information into our classical trajectories by slightly adjusting the parameters that describe the classical model (only in the region where the relevant new information applies). Whichever viewpoint is more applicable might depend somewhat on one's personal preferences, but also on just how much the classical parameters had to be readjusted. For small changes, this second viewpoint is very appealing, but if the quantum region requires an alteration that is very drastic and different at every time step, it seems to us more intuitive to talk about interpolation.

- The scheme uses a time–dependent Hamiltonian to carry out the dynamics, and thus energy is not conserved. Although this is not a logical consequence of the above, nevertheless we have not yet found a formulation which obeys strict energy conservation when the quantum region changes during the simulation, i.e. when atoms regularly cross from the quantum to the classical region and vice versa. In practice a thermostat is used to absorb any small drift. This works well except for problems where heat exchange with a bath directly affects what we want to measure, e.g. relative enthalpies.

- The parameter tuning of the universal Hamiltonian need not necessarily be carried out at every time step. One can use the same parameters for a small number of steps, and only then compute the forces with the expensive quantum mechanical model, which are then used to retune the parameters. This procedure can be formalized in a predictor–corrector scheme as follows. From a point $\mathbf{R}^0$ in phase space, having parameters α^0 (let us denote this by $(\mathbf{R}^0, \alpha^0)$, make a number of MD steps to arrive at point $(\mathbf{R}^1, \alpha^0)$. Here, quantum calculations and optimization takes place, so having got new parameters we are at $(\mathbf{R}^1, \alpha^1)$, this is the end of the "predictor" part. The MD could be continued from this point, but then the trajectory would suffer an abrupt change in its second derivative, because of the discontinuity in the Hamiltonian parameters, α. So instead, we go back to the previous point $(\mathbf{R}^0, \alpha^0)$ and redo the dynamics, interpolating the parameters between α^0 and α^1. At the end of the interpolation we arrive at a slightly different point in phase space, $(\mathbf{R}^2, \alpha^1)$, completing the "corrector" part. The cycle could be repeated by recomputing the quantum mechanical forces, getting new parameters α^2 and going back to $(\mathbf{R}^0, \alpha^0)$ to reinterpolate. In practice, we limit ourselves to one cycle, thereby ensuring a continuous variation of the parameters along the trajectory.

- The alternative viewpoint above highlights a possible computational simplification. Far away from the quantum region, the potential parameters would not be changing very much

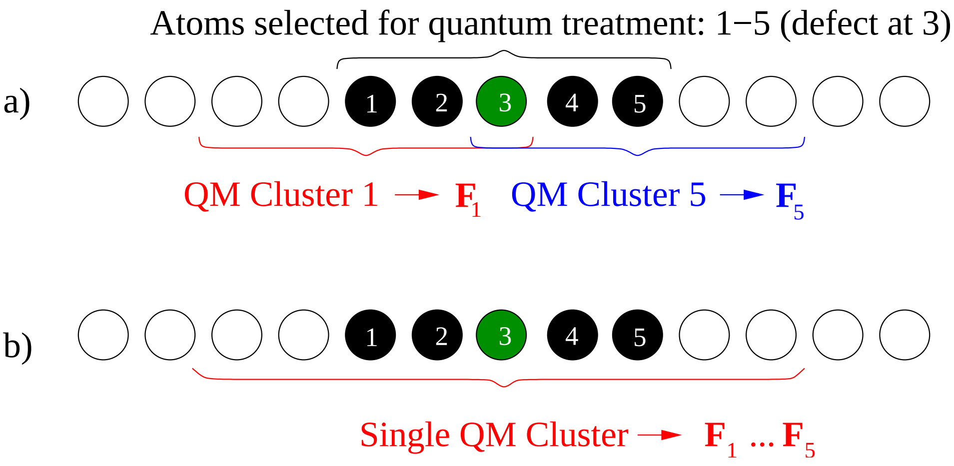

Figure 1: Given a region of interest, e.g. a point defect (green), we declare that this and other atoms within a certain distance should be treated with quantum mechanical accuracy (black). There are two ways of computing the accurate forces that we use in the fitting process, a) by carving a temporary cluster separately for each QM atom, and keeping only the force on the central atom from each QM calculation, or b) by computing a *larger* cluster quantum mechanically, and only keeping the forces on the originally selected QM atoms, discarding the forces near the (artificial) surface.

(or at least the precise details of the trajectories of far–away atoms do not affect processes in the quantum region due to strong locality). So they might as well be left as they are, and not included in the parameter optimization. This speeds up the optimization by a significant factor. If we have several quantum regions which are well separated, the optimization of the parameters near each region could be carried out in parallel.

- Because of strong locality, the forces on the atoms even in the quantum region can be computed independently. To do this, for each required atom, one carves out a spherical cluster centered on the given atom, and computes the forces, retaining only the force on the central atom (see Figure 1a). This temporary cluster can be chemically terminated (e.g. by hydrogen atoms) on the surface for improved accuracy (or smaller cluster radius for any given accuracy). This termination is not strictly necessary, but makes for a faster algorithm. We emphasize that the boundary of these clusters plays a very different role from the boundary of the quantum region which causes a lot of the difficulties in the traditional embedding schemes. Because each cluster calculation is independent, they can be carried out in parallel requiring minimal bandwidth for inter–processor communication. This possibility makes the scheme particularly suitable for running on massively parallel computer–farms, which are typically connected by a comparatively slow communication network.

  One can always fall back on a single large quantum mechanical calculation, as depicted in Figure 1b. The cluster should then be large enough that the forces on atoms near its boundary can be discarded (ie not used in the parameter optimization), thus again avoiding the problems that the introduction of an artificial surface might lead to.

Let us review the approximations that the scheme involves. Firstly, somewhat trivially, parts of the system are treated with a less accurate classical model. This is a controllable approximation, since the size of the quantum mechanically treated region can be varied at will; this can be done in all embedding schemes. We expect a smooth variation of physical observables as the size of the quantum region is varied because the changing boundary of the quantum region does not bias the calculation: information coming from near the surface of the temporarily carved clusters is thrown away (see Figure 1). Secondly, if we compute quantum mechanical forces using separate clusters, the force on the central atom should be converged with the cluster radius, or at least the error should be within acceptable limits. For example, even in a first principles *ab initio* quantum mechanical calculation, if we do not expect to get forces more accurately than 0.1 eV/Å, it would be a waste of effort to converge to better than this with the cluster radius. The same consideration sets the target accuracy of the parameter optimization of our universal Hamiltonian. Below we give typical errors for all these approximations.

Although we lost the ability to do strictly microcanonical simulations, this is offset by other gains. The generality of the force–fitting means that any quantum engine can be plugged into the algorithm as a black box, without a need to alter the software. All physical observables can be computed from the MD trajectories, and we expect successes in problems where finite temperature is important, and the controlling quantity is the free energy. Moreover, since averages from different thermodynamical ensembles approach each other in the limit of large samples, long time averages from non–microcanonical molecular dynamics trajectories are just as good as those from microcanonical runs.

It turns out that the present scheme allows us to make the QM region very small and mobile, i.e. we can continuously select which atoms to treat more accurately during the simulation. This brings the obvious benefit of making the calculations run faster, but highlights the need for robust algorithms for determining where the QM region should be. It is clear that this will depend on the nature of the scientific question one is asking. It is not in general possible to correct the classical trajectories everywhere they go wrong, since tests show that even at modest displacements from equilibrium, classical models may predict forces that are wrong by as much as 1 eV/Å as compared with quantum mechanical forces.

In practice, this means that, for solid phases, the selection of the quantum region has to be implemented using geometric and topological criteria. For this, we found it advantageous to keep a running average of atomic positions to filter out the fast optical phonons, and assess the local geometry based on the these averaged positions,

$$\tilde{\mathbf{x}}(t) \equiv \frac{1}{1/2 + \tau/\Delta t} \sum_{n=0}^{\infty} e^{-n\Delta t/\tau} \mathbf{x}(t - n\Delta t), \tag{9}$$

where Δt is the time step of the molecular dynamics, and τ is the time–constant of the averaging. We found the averaged coordinates are very well suited to finding the location of point defects and locating bonds that are being broken.

We now present each step of the scheme in order, indicating numerical values for parameters that we have been using. For the sake of concreteness, we take as an example the diffusion of a vacancy in crystalline silicon. This is not a problem which a priori stands out as needing an embedded simulation, but precisely because of this, it can provide validation.

1. **Initialization** Start with the a 3x3x3 cubic unit cell (215 atoms and a vacancy), with

atoms near their bulk equilibrium positions, and with a reasonable choice of initial parameters for the classical potential, in our case we choose the Stillinger–Weber potential[5]. The velocities are randomized and rescaled to the simulation temperature, after which a thermostat is used to maintain an NVT ensemble.

2. **Extrapolation** As in standard molecular dynamics (MD), use the potential with fixed parameters to generate five 1 fs time steps of the system trajectory using the velocity Verlet algorithm.

3. **Testing** In the latest configuration, the local validity of the classical potential needs to be assessed on a site by site basis, and a selected subset of atoms is flagged for quantum treatment. As discussed above, this selection cannot be made fully automatically, because it depends on the scientific question being asked. Presently we are interested in the diffusion of a point defect, so it is natural to describe the region surrounding the defect quantum mechanically. To identify where the vacancy is, we use equation (9) with a time–constant of 100 fs, and match the averaged atomic coordinates with their nearest lattice points. Having located the site of the missing atom, we flag all atoms that are within 7.5 Å of its lattice point (about 100 atoms).

4. **Quantum mechanical calculations** We compute accurate forces on all flagged atoms using an empirical tight binding method[6] and the carved–cluster approach described above. The cluster radius is set to 7 Å, this yields about 150 atoms in each cluster, including terminating hydrogens. The termination atoms are put in place of the Si atoms that fell just outside of the given cluster and their positions are adjusted to the equilibrium Si–H distance along the direction of each Si–Si bond that was cut. The Hellman–Feynman force on the central atom is then computed after a direct diagonalization of the Hamiltonian. This force is shown to converge quickly with cluster radius and to be relatively insensitive to the precise termination strategy. We determined in a separate test (0.5 ps LOTF simulation of a vacancy diffusion event at 1400K) that a 7 Å radius is enough so that the RMS deviation from the the exact TB forces (computed with periodic boundary conditions) is < 0.1 eV/Å. Constructing clusters of similar size including all Si atoms up to a chosen neighbour shell rather than up to a fixed radius yields analogous results.

5. **Force fitting** We tune the parameters of the classical potential until it reproduces the accurate forces, by minimizing (8) using the conjugate gradients technique. The starting values for the parameters are always reset to be the same as those of original unmodified potential. For atoms that do not have a quantum mechanical force calculated on them, the current classical force is used as the target of the optimization. Note that we require the evaluation of the classical potential for a large number of different parameters sets, all at the same atomic configuration. We have devised special routines that reformulate the potential to be of the form

$$E = M_0(\mathbf{R}) + M_1(\mathbf{R})\alpha + M_2(\mathbf{R})\alpha^2,$$

where only the matrices M_i depend on the atomic coordinates and are computed once before the optimization starts; α and α^2 indicate the vector of the parameters and their

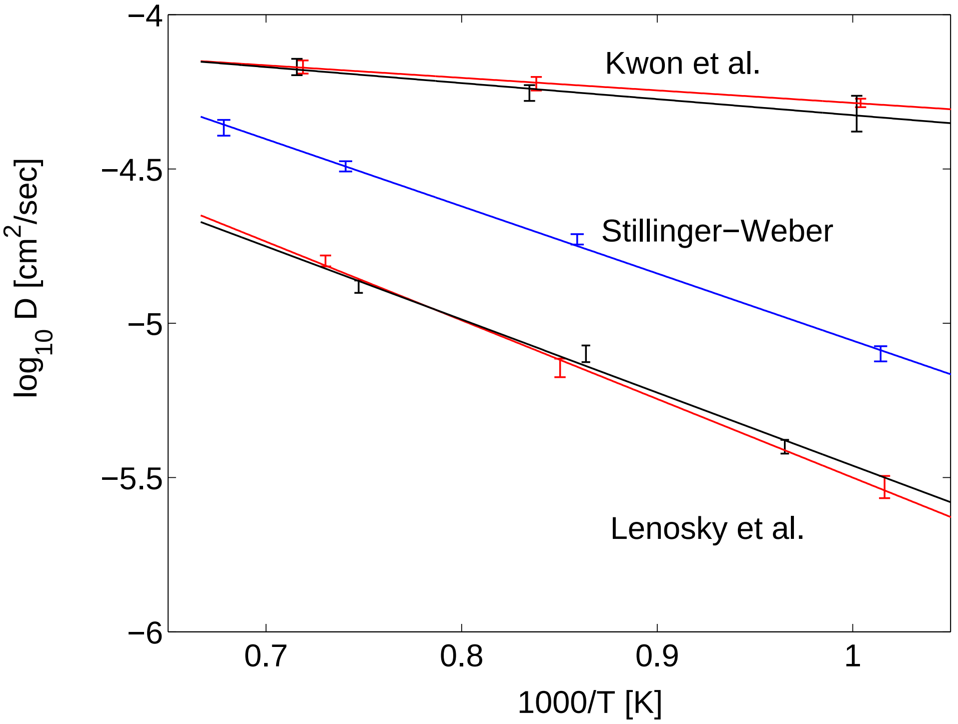

Figure 2: Arrhenius plot of the silicon vacancy diffusivity obtained by the present scheme fitted "on the fly" on different TB models (red), compared with the results of fully TB simulations (black) and fixed-parameter SW potential (blue).

squares, respectively. The forces can be written in a similar way and thus during the optimization, most of the CPU time is spent in BLAS libraries. Tests show that parameters related to atoms which are further than a few neighbour shells outside the QM region do not change appreciably with the fit. The optimization is therefore limited to the two–body and three–body terms of the potential involving atoms in a spherical region of 12 Å radius centered on the diffusing defect. About 30 conjugate gradient steps are sufficient to perform a converged fit, the maximum residual deviation from the target forces being typically less than 0.01 eV/Å.

6. **Interpolation** Now return the state of the system to that before the extrapolation and rerun the dynamics, interpolating the potential parameters between the old and the new values. We use a cubic spline interpolation, so the time–derivatives of the parameters are zero at the fit–points.

7. **Return to 2.**

4 Validation

Using this procedure, we computed the diffusivity for the Si vacancy[7] by running a 1 ns constant temperature (CT) simulation of a 215 atom periodic system at $T = 1400$K and obtained a value of $(2.1 \pm 0.4) \times 10^{-6}$ cm^2/sec. This compares well with the value of $(2.3 \pm 0.2) \times 10^{-6}$ cm^2/sec, calculated using the (same) tight binding scheme[6] for the full system. For comparison, the Stillinger–Weber potential gives $(3.4 \pm 1.0) \times 10^{-5}$ cm^2/sec), a much larger value. It must be

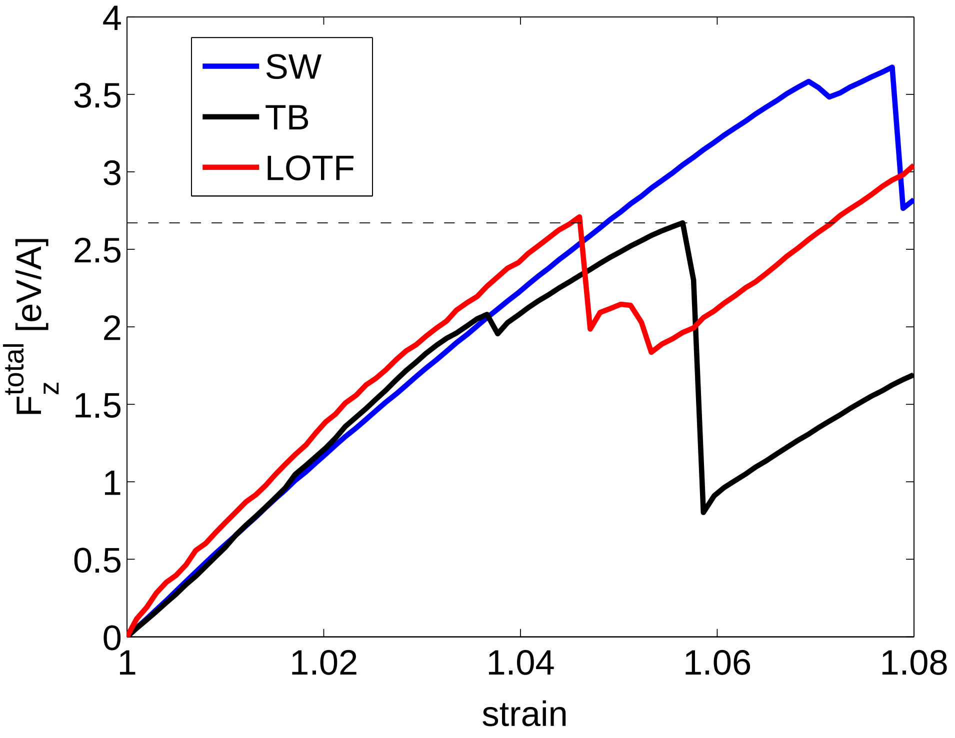

Figure 3: Stress–Strain curves of a silicon nanobar with a vacancy, using three different methods: Stillinger–Weber (blue), tight–binding (black), and LOTF(red).

stressed that the diffusivity is a quantitative test of the embedding method, and should not be taken to be an application where embedding is really necessary. A 215 atom silicon system is most efficiently simulated by standard techniques.

This is even more true of our next test, where we look at the temperature dependence of the vacancy diffusivity. To enable the large number of runs that a good comparison requires, we have chosen to use a 2x2x2 cubic unit cell with 63 atoms. Here, the quantum forces used for the parameter fitting in the LOTF run were calculated using the full periodic periodic system, rather than with clusters.

Figure 2 shows our results for the vacancy diffusivity in Si as a function of temperature, obtained by CT simulations using the fixed–parameter SW potential, two different TB schemes[8, 9] and our hybrid LOTF scheme. We note that the large difference between the results obtained by fitting the scheme on the two different quantum models is due to the different predictions of these models in accurate quantitative computations, and faithfully reproduced by the hybrid method. This emphasizes the fact that the present scheme can at best be expected to reproduce the results of the QM model that it is given, but can in no way improve its accuracy.

A different quantitative test is provided by the example of stressing a silicon nanobar. Starting with a 2x2x10 supercell of the cubic unit cell, we introduce a vacancy, and relax the structure to equilibrium. Then the atomic coordinates are rescaled parallel to the bar axis, and again relaxed to equilibrium while holding the ends fixed. In the hybrid simulation, the QM region included atoms within 4 Å of the vacancy. In this case, rather than using clusters, the tight–binding forces were calculated by considering a cluster that was a bit larger than the QM region (by 5 Å on each side), and again terminated with hydrogen atoms where bonds were broken in the construction of the cluster.

Figure 3 shows the resulting stress–strain curves (the sum of the z components of the forces on the fixed atoms at one end of the bar is proportional to the stress). The hybrid simulation and the fully quantum simulation give the same critical stress level (dashed line) at which the bar fails mechanically near the vacancy, while the classically computed critical stress is significantly higher. This example also illustrates that the microscopic trajectories are, of course, not necessarily reproduced: the curves have minor jogs and kinks due to small changes in the surface reconstruction of the nanobar, which do not affect the critical stress.

5 Brittle failure

Having validated our scheme in small systems where it was possible to compute observables using a fully quantum mechanical method, we now turn to a system which has been epitomized as the benchmark for hybrid schemes, brittle failure of covalent crystals. When single crystals of silicon or diamond are strained beyond breaking point, they relieve the stress by opening cracks. A universal observation is that these cracks are atomically sharp and the resulting newly opened surfaces are almost atomically flat[10]. The system is evidently multiscale, and the behaviour on the different lengthscales are highly correlated: the large stress concentration near the crack tip induces the breakage of atomic bonds, and it is the successively broken bonds that let the crack tip (and the stress field) advance forward as the crack propagates.

To date, all purely classical simulations have failed to reproduce a basic feature of the system, namely that the cracks tips remain atomically sharp as the crack opens. This is principally due to the overestimation of lattice trapping effects[11], which results in an excess of applied stress with respect to the critical value to get the crack moving in the first place. This excess of elastic energy is dissipated by tip blunting and local melting.

Other efforts at developing hybrid schemes have also concentrated on cracks[3]. The principal advantages of our scheme is that the quantum region can be made very small (300-600 atoms for a silicon crack tip) and is allowed to follow the tip as the crack propagates, resulting in a computational speedup without compromising the accuracy of the calculation.

Figure 4 shows three snapshots of our simulation of the $(111)[1\bar{1}0]$ crack system, as it propagates in the $[11\bar{2}]$ direction at 0 K. We used the *ab initio* SIESTA[12] package to treat atoms in the moving quantum region. Apart from showing smooth atomically flat surfaces opening, using such a sophisticated QM engine revealed that the surface reconstruction is different on the upper and lower surfaces, with the upper surface showing the 2×1 Pandey reconstruction, as indicated by the alternating pentagons and heptagons. The reason why only one surface shows this reconstruction can be understood by considering the dynamics of atoms near the crack tip. The atoms, shown in black, that were part of a hexagon are forced towards each other as the crack tip passes, thus driving the formation of a pentagon. The corresponding atoms on the lower surface (shown in gray) are forced away from each other, preventing pentagon formation.

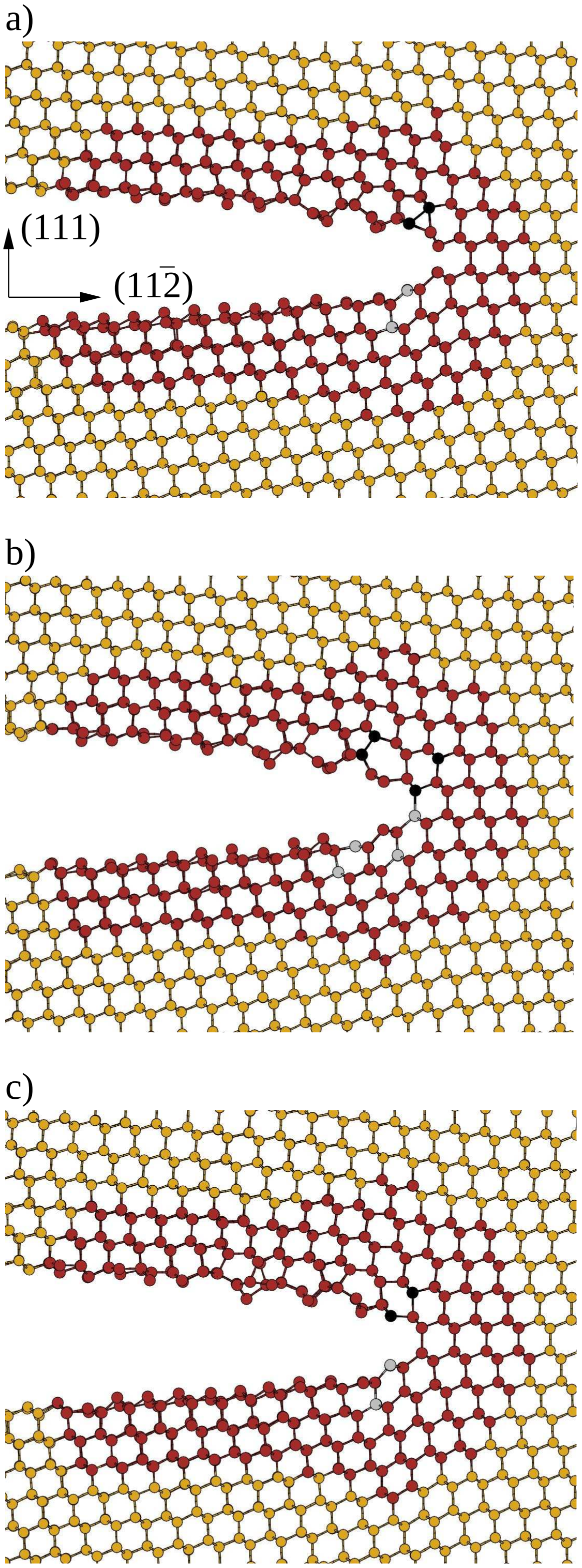

Figure 4: Three snapshots of the opening (111)[1$\bar{1}$0] crack system simulated using LOTF. Atoms in red were treated quantum mechanically using the *ab initio* SIESTA package. The quantum region follows the crack tip as it moves from left to right. Note the pentagons and heptagons of the 2 × 1 Pandey reconstruction on the top surface. See text for an an explanation of the dynamical aspects.

References

[1] R. M. Nieminen, J. Phys. Cond. Mat. **14** 2859 (2002).

[2] E. B. Tadmor *et al.* Philos.Mag. **73** 1529 (1996) ; E. B. Tadmor *et al.*, Langmuir **12** 4529 (1996).

[3] F.F.Abraham *et al.*, Comp.Phys. **12**,538 (1998); F.F.Abraham *et al.*, Mat. Res. Soc. Bulletin **25**, 27 (2000); C. L. Rountree *et al.* Annu. Rev. Mater. Res. **32** 377 (2002); S. Ogata *et al.* J. Appl. Phys. **95** 5316 (2004); S. Ogata and R. Belkada, Comp. Mat. Sci. **30** 189 (2004).

[4] Gábor Csányi *et al.*, Phys. Rev. Letts **93** 175503 (2004); A.DeVita and R.Car,MRS Symp.Proc. **491**,473 (1998).

[5] F.Stillinger and T.Weber,Phys.Rev.B **31**,5262 (1985).

[6] D.R.Bowler *et al.*, J.Phys.Cond.Matt. **10**, 3719 (1998).

[7] M.Tang *et al.*, Phys.Rev.B **55**, 14279 (1997).

[8] I.Kwon *et al.*, Phys. Rev. B **49**, 7242 (1994).

[9] T.J.Lenosky *et al.*, Phys. Rev B **55**, 1528 (1997).

[10] S. Kohlhoff *et al.*, Phil.Mag.A**64**,851 (1991).

[11] N. Bernstein and D. W. Hess, Phys. Rev. Lett. **91**, 025501 (2003).

[12] D.Sanchez-Portal *et al.*, Int.J.Q.Chem. **65**,453 (1997).