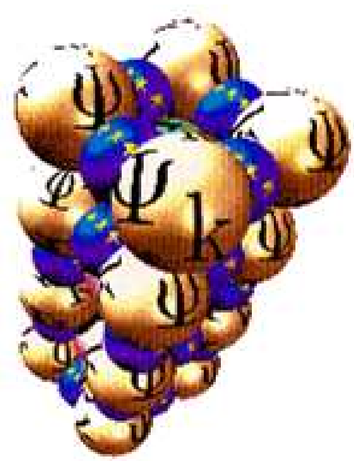
Ψ_k Newsletter

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

Number 77 October 2006



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Sponsored by: UK's CCP9
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Contents

1 Editorial

In this newsletter we have a very nice scientific highlight by Derwyn A. Rowlands (University of Bristol, UK) on "Short-range correlations in disordered systems: the Non-Local Coherent-Potential Approximation (NL-CPA)". It is an up to date critical review of the non-local CPA by one of its originators. In addition, as usual the newsletter contains a number of abstracts of newly submitted and recent papers, announcements of meetings and available positions, and two workshop reports, with abstracts of presented talks. In particular, note please that in this newsletter we have the first announcements of three graduate schools, organized between December 2006 and summer 2007 within the EU-sponsored Psi-k Training. 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 2006 workshops and hands-on courses (subject to funding).

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

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2 News from the ESF Programme

”Towards Atomistic Materials Design”

2.1 Reports on the ESF Psi-k Programme Workshops/Conferences

2.1.1 Report on International Workshop and School on "TIME DEPENDENT DENSITY FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS"

2006, August 27 – September 11

A. Rubio (Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and DIPC),
E. K. U. Gross (Freie Universität Berlin),
M. A. L. Marques (Universidad de Coimbra, Portugal and ETSF-UPV//EHU),
F. Nogueira (Universidad de Coimbra and Centro de Física Computacional)

SPONSORED BY:
NANOQUANTA Network of Excellence
ESF Psi_k Programme
CECAM
Spanish Ministry of Science and Technology
Benasque Center for Science
Universities of the Basque Country and Coimbra
HP and IBM computer support

The School and workshop was hosted by the Benasque Center for Science, located at the heart of the Pirinees. The aim of the school was to introduce theoretical, practical, and numerical aspects of Time-dependent-density functional theory (TDDFT) to young graduate students, post-docs and even older scientists that are envisaging a project for which TDDFT would be the tool of choice. During the school we incentivated a close and informal contact between the students and the teachers. Furthermore, the students presented their current research activities and future interests (six of those presentations were selected as oral contributions to the international workshop). We felt that this was an important point, since young scientists should be involved in the building up of a strong community. The number of applications (above 190) surpassed all expectations and, of course, the limit of 43 places that we had to satisfy in order for the students to get the maximum benefit from the school, and also due to space and computer resource limitations. The students (graduate and postgraduate) also did participate in the workshop held just after the 10 days of school. The total number of participants was 90 from all over the world (including 16 females; three as invited speakers/lectures). The distribution was:

	Organizers	Teachers	Students	Invited	Participants	School	Workshop
Australia	0	0	0	0	1	0 1	
Austria	0	0	3	1	0	3	4
Belgium	0	1	1	1	0	2	3
Brazil	0	0	2	0	0	2	2
Chile	0	0	1	0	0	1	1
Finland	0	0	3	1	0	3	3
France	0	3	2	4	1	5	7
Germany	1	4	5	7	1	9	16
Holland	0	1	3	1	0	4	5
Iran	0	0	3	0	0	3	3
Israel	0	0	0	1	0	0	1
Italy	0	1	4	3	1	5	8
Japan	0	0	0	1	1	0	2
Mexico	0	0	2	0	1	2	3
Portugal	2	3	3	0	1	6	7
Spain	1	3	3	1	0	6	7
Sweden	0	0	2	0	0	2	2
Switzerland	0	0	0	2	0	0	2
UK	0	1	0	1	2	1	3
USA	0	1	6	3	1	7	10
TOTAL	4	18	43	27	10	61	90

The aim of the Workshop was to assess the present status of TDDFT approaches to the study of spectroscopic properties of real materials, and explore their capability for applications in further systems with technological and biological interest. The recent developments of TDDFT covered during the workshop include TDDFT versus current-DFT, van der Waals interactions, applications to biological systems, new functionals, transport phenomena, optical spectra of solids , etc. Due to the different methods used to tackle this problem (Many-Body Theory, Density Functional Theory, Configuration Interaction, semi-empirical approaches), this Workshop was intended as a way to promote links among scientists coming from different communities working or interested in electron excited states. Also it was intended as a follow-up event for the students attending the school as it was a good opportunity for them to see the real implications of the school lectures and get the new theoretical advances in the the development of exchange-correlation functionals as well as applications to complex systems (nanostructures, bio-molecules, interstellar molecular analysis, solids, etc.) Our goal was to bring together scientists working on foundations and different applications of TDDFT and many-body theory, trying to assess the capability of current approximations to be applied to real systems of increasing complexity. The invited and contributed talks covered:

I) Fundamental topics on TDDFT, Many-Body Theory, and electron transport theory.

II) New approximations and techniques.

III) Ab-initio calculations of spectroscopic properties of complex materials.

As a consequence, there was a broad variety of participants which helped to get an interdisciplinary vision of the field. Thus, although some of the more specific topics were far from the research interest of many participants, the meeting was an excellent opportunity to see how the same techniques are used by members of other communities.

School Program

Day	**Hour**	**Title**	**T/P**
28/8	9:30 - 11:00	TDDFT I - Introduction (EG)	T
	11:30 - 13:00	TDDFT II - Linear Response Theory (EG)	
	15:00 - 18:30	Introduction to the practical classes (codes Octopus, Self, Abinit) (MM+AM+YP)	P
29/8	9:30 - 11:00	TDDFT as a tool in chemistry I (FF)	T
	11:30 - 13:00	TDDFT III - Strong Fields (EG)	
	15:00 - 18:30	Quantum Dots I (AC+MM+MO+FN)	P
30/8	9:30 - 11:00	Many-Body I - Introduction (RG)	T
	11:30 - 13:00	TDDFT as a tool in chemistry II (FF)	
	15:00 - 18:30	Quantum Dots II (AC+MM+MO+FN)	P
31/8	9:30 - 11:00	Many-Body II - GW and BSE (RG+LR)	T
	11:30 - 13:00	TDDFT IV - Keldish formalism (RvL)	
	15:00 - 18:30	Quantum Dots III (AC+MM+MO+FN)	P
1/9	9:30 - 11:00	Many-Body III - Many-Body vs TDDFT (LR)	T
	11:30 - 13:00	Propagation schemes (AC)	
	15:00 - 18:30	OCTOPUS I (FN+MO+MM+AC)	P
2/9		Free (excursion to be announced)	
3/9	9:30 - 11:00	TDDFT V - Advanced topics I (RvL)	T
	11:30 - 13:00	Models for time-dependent phenomena I (ML)	
	15:00 - 18:30	OCTOPUS II (FN+MO+MM+AC)	P
4/9	9:30 - 11:00	TDDFT VI - Advanced topics II (RvL)	T
	11:30 - 13:00	Models for time-dependent phenomena II (ML)	
	15:00 - 18:30	ABINIT+SELF I (AM+LW+MB+PG+SB+YP)	P
5/9	9:30 - 11:00	TDDFT as a tool in biophysics (AR+MM)	T
	11:30 - 13:00	Nonadiabatic electron dynamics in TDDFT I (CU)	
	15:00 - 18:30	ABINIT+SELF II (AM+LW+MB+PG+SB+YP)	P
6/9	9:30 - 11:00	Nonadiabatic electron dynamics in TDDFT II (CU)	T
	11:30 - 13:00	Challenges in TDDFT and Final remarks (AR)	

Lecturers for the theoretical classes

	Lecturer
AC	Alberto Castro (FU Berlin, Germany)
AR	Angel Rubio (San Sebastian, Spain)
CU	Carsten Ullrich (Missouri, USA)
EG	E. K. U. Gross (FU Berlin, Germany)
FF	Filipp Furche (Karlsruhe, Germany)
LR	Lucia Reining (Paris, France)
ML	Manfred Lein (MPI Heidelberg)
MM	Miguel Marques (Coimbra, Portugal)
RG	Rex W. Godby (York, UK)
RvL	Robert van Leeuwen (Groningen, The Netherlands)

Tutors for the practical classes

	Tutor
AC	Alberto Castro (FU Berlin, Germany)
AM	Andrea Marini (Rome, Italy)
FN	Fernando Nogueira (Coimbra, Portugal)
LW	Ludger Wirtz (Lille, France)
MB	Michel Bockstedte (San Sebastian, Spain)
MM	Miguel Marques (Coimbra, Portugal)
MO	Micael Oliveira (Coimbra, Portugal and San Sebastian, Spain)
PG	Pablo Garcia (Madrid, Spain)
SB	Silvana Botti (Paris, France)
YP	Yann Pouillon (Louvain-la-Neuve, Belgium)

Workshop

Workshop Program

Day I: Thursday 7th		
09:00	Hardy Gross	Opening remarks
09:10	Neepa Maitra	Some challenges for time-dependent density functional approximations - and some partial solutions
10:00	N. Lathiotakis	Reduced density matrix functionals for finite and periodic systems
10:50	Caffeine break	
11:20	Mark Casida	Two-electron excitations in TDDFT
12:10	Stephan Kummel	Strong-field excitations and derivative discontinuities in TDDFT
13:00	Lunch break	
15:00	E. J. Baerends	Avoided crossings of excited state surfaces and vibronic coupling in TDDFT
15:50	Ivano Tavernelli	Non-adiabatic TDDFT MD: from gas phase to complex environments
16:40	Caffeine break	
17:10	Juerg Hutter	TDDFT calculations with the Gaussian augmented plane wave approach
18:00	Rodolfo del Sole	Calculation of optical properties of complex systems within TDDFT
18:50	Dmitrij Rappoport	Practical aspects of molecular TDDFT calculations
Day II: Friday 8th		
09:10	Andreas Goerling	Exact exchange spin current density functional methods
10:00	Myrta Grüning	The effect of nonlocality on the band gap within density functional theory
10:50	Caffeine break	
11:20	Matteo Gatti	Nonlocality and frequency dependence of effective potentials
12:10	Rex Godby	Exchange-correlation functionals and kernels for conductance and polarization
13:00	Lunch break	
15:00	Massimiliano di Ventra	Transport in nanoscale systems: new approaches to an old problem
15:50	Gianluca Stefanucci	Time dependent transport phenomena within TDDFT
16:40	Beer break	
17:10	Carsten Ullrich	Time-dependent generating-coordinate method
18:00		Poster session, cheese and wine

Day III: Saturday 9th		
09:10	Eckhard Pehlke	Molecular dynamics simulations of non-adiabatic processes
10:00	Roi Baer	Nonadiabatic functionals and their effects on electron dynamics in molecules and metal clusters
10:50	Caffeine break	
11:20	Esa Räsänen	Optimal laser control of quantum rings
12:10	Silvana Botti	How do rewritable DVDs work: optical properties of phase-change materials
13:00	Lunch break	
15:00	Ludger Wirtz	Electronic excitations in hexagonal layered systems (C and BN)
15:50	Deborah Prezzi	The role of excitons in the optical properties of carbon nanotubes
16:40	Beer break	
17:10	Marti Pi	TDDFT description of electronic systems in semiconductor heterostructures
18:00		Oral presentation of the best posters
Day IV: Sunday 10th		
09:10	Stefano Baroni	Turbocharging time-dependent density-functional theory with Lanczos chains
10:00	Yoshi Miyamoto	TDDFT-MD simulation of nano-carbons: decay dynamics of hot-carriers and electronic shakeup by high-speed ions/atoms
10:50	Caffeine break	
11:20	Patrick Rinke	The band gap of InN and ScN: a quasiparticle energy study based on exact-exchange density-functional theory
12:10	C Ambrosch-Draxl	The role of core states on the excitation spectra of solids
13:00	Angel Rubio	Closing remarks

Abstracts

Some challenges for time-dependent density functional approximations - and some partial solutions

Neepa T. Maitra

Hunter College of the City University of New York

The burst of activity and applications using TDDFT is evidence of its remarkable success in predicting a range of phenomena for a wide range of systems. The simple functional approximations, bootstrapped from ground-state approximations, appear to fare very well in the general case. There are however exceptions where these functionals fail, and where challenges lie in the development of more accurate functionals. I will discuss three very different cases, and offer partial solutions for them. First, excitations of a long-range heteroatomic molecule composed of open-shell units. Both local and charge-transfer excitations require strong non-adiabaticity in the exchange-correlation kernel. These excitations are necessary to get right if TDDFT is to be used for potential energy curves in electron-ion dynamics involving dissociation, for example. A key feature of this problem is step structure in the exact ground-state potential, which eludes the usual (semi-)local LDA/GGAs, and even exact exchange. A new approach that extracts a ground-state potential from the Vignale-Kohn current-density response functional will be shown to capture the steps well for the closely-related problem of homoatomic species in electric fields. Second, in strong-field dynamics, the underlying single Slater-determinant nature of the Kohn-Sham wavefunction is at the root of severe difficulties particularly important in attosecond quantum control problems. To treat this, initial work towards a new extension of the theory to phase-space density functionals will be presented. Finally, time allowing, the question of whether the presently available TDDFT approximations can capture quantum chaos induced by electron-electron interaction alone will be addressed.

Reduced density matrix functionals for finite and periodic systems

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Reduced Density Matrix Functional Theory (RDMFT) is based on Gilbert's theorem, which guarantees that every observable is a functional of the one-body-reduced density matrix (1-RDM). We discuss several aspects of RDMFT, review its application to finite systems and finally, we emphasize on its application to periodic systems. The implementation of 1-RDM functionals for periodic systems is based on a Wannier- or Bloch-states description of the system. In a similar fashion to DFT, we explore the possibility of using the discontinuity of the chemical potential as a measure of the fundamental gap. Finally, we apply last generation functionals of the 1-RDM to the case of the Homogeneous Electron Gas (HEG). It is demonstrated that they offer a better description than their predecessors. In addition, by using suitable fitting parameters, we show that the exact correlation energy of the HEG can be reproduced. The derivative functionals are expected to be useful in the application of RDMFT to metallic systems.

Polarization Propagator Corrections to Linear Response Time-Dependent Density-Functional Theory for Molecules with Closed- and Open-Shell Ground States

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http://www-ledss.ujf-grenoble.fr/PERSONNEL/LEDSS7/casida/FRAMES

A decade ago time-dependent density-functional theory (TDDFT) was introduced to the quantum chemistry community in its linear response (LR) for calculating excitation spectra [C95]. Since that time LR-TDDFT has become a method of choice for calculating molecular vertical excitation energies because of its demonstrated accuracy within the domain of applicability [C01] determined by present-day approximate exchange-correlation functionals. One limitation of the method comes from the wide-spread use of the TDDFT adiabatic approximation which limits LR-TDDFT to quasiparticle spectra (i.e., one-electron excitations). Two-electron excitations are important when calculating the excitation energies of closed-shell molecules both (i) because of the importance in some molecules of excited states with substantial two-electron character and (ii) because the inclusion of two-electron excitations allows a better description of biradical ground states. Spin-flip excitations are a particular type of two-electron excitation which is important for a correct description of the excitation spectra of molecules with open-shell ground states. Some of these points are nicely illustrated in Ref. [CIC06]. In this talk I plan to outline how the equation-of-motion superoperator approach may be used to derive nonadiabatic polarization propagator corrections [C05] to adiabatic LR-TDDFT for application to the above mentionned problems.

[CIC06] M.E. Casida, A. Ipatov, and F. Cordova, in *Time-Dependent Density-Functional Theory*, edited by M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, and E.K.U. Gross, *Lecture Notes in Physics* (Springer: Berlin, 2006). “Linear-Response Time-Dependent Density-Functional Theory for Open-Shell Molecules”

[C05] M.E. Casida, J. Chem. Phys. **122**, 054111 (2005). “Propagator Corrections to Adiabatic Time-Dependent Density-Functional Theory Linear Response Theory”

[C01] M.E. Casida, in *Accurate Description of Low-Lying Molecular States and Potential Energy Surfaces*, ACS Symposium Series 828, edited by M.R. Hoffmann and K.G. Dyall (ACS Press: Washington, D.C., 2002), p. 199. “Jacob‘s ladder for time-dependent density-functional theory: Some rungs on the way to photochemical heaven”

[C95] M.E. Casida, in *Recent Advances in Density Functional Theory*, Vol. I, edited by D.P. Chong (World Scientific: Singapore, 1995), p. 155. “Time-dependent density-functional response theory for molecules”

Preprints of Refs. [C95], [C01], and [CIC06] may be downloaded from

http://www-ledss.ujf-grenoble.fr/PERSONNEL/LEDSS7/casida/research/complete.html

Strong-field excitations and derivative discontinuities in time-dependent density functional theory

Stephan Kümmel

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Time-dependent density functional theory with local or semi-local approximations for the exchange-correlation potential has been quite successful in the linear response regime. However, non-linear, non-perturbative excitations like the ionization of finite systems by strong laser fields are not well described by approaches like the adiabatic local density approximation (ALDA). We argue [1] that this failure is due to the fact that in time-dependent Kohn-Sham theory, there is an analog of the particle-number discontinuity that is well known in ground-state Kohn-Sham theory [2]. This discontinuity is missing in approaches like the ALDA. We demonstrate the importance of this discontinuity by calculating the exact (within numerical limits) time-dependent exchange-correlation potential for an ionization process. Finally, we discuss in how far this discontinuity can be incorporated into Kohn-Sham theory via the time-dependent optimized effective potential formalism.

[1]M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005);
M. Mundt and S. Kümmel, Phys. Rev. Lett. **95**, 203004 (2005).
[2]J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

Avoided crossings of excited state surfaces and vibronic coupling in TDDFT

E. J. Baerends

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Time-dependent DFT has become a very powerful tool in spectroscopical investigations in chemistry for several reasons.
In the first place, it is remarkably accurate, if sufficiently accurate (not LDA or GGA but “shape-corrected”) Kohn-Sham potentials are used. Approximations to the exchange-correlation kernel are much less critical, the adiabatic LDA usually suffices.
In the second place the Kohn-Sham orbitals and the orbital energies are physically meaningful, much more so than the Hartree-Fock orbitals. The occupied orbital energies are very close to ionization energies, and unoccupied-occupied orbital energy differences represent to very good approximation excitation energies. Moreover, excitations are often represented for more than 90% by single orbital excitations, affording very s traightforward interpretation of excitation spectra.

The accuracy of the TDDFT excitation energies is such that it should be sufficient to describe properly the potential energy curves even in regions of avoided crossings. This poses the questions whether it would be possible to calculate non-Born-Oppenheimer effects (vibronic coupling) with TDDFT. The crucial step is that one needs a so-called diabatization method to extract from the calculated adiabatic excited state surfaces properly diabatized surfaces, and coupling constants. A method for calculating vibronic coupling will be discussed.

This vibronic coupling method has been implemented in the ADF TDDFT code. We will discuss two applications. The first is to N_2.
The N_2 excitation spectrum has proved surprisingly difficult to calculate correctly, partly because of a crossing of the three lowest excited states of $^1\Pi_u$ symmetry. The ordering of these states at R_e has been incorrectly given, compared to the standard experimental assignment, in many recent *ab initio* and all TDDFT calculations. This has led to the suggestion that the experimental assignment might have to be revised. However, using the vibronic coupling to obtain fully comparable theoretical and experimental spectra, we can rule out this possibility and we have to conclude that the excitation energy for one of the

$^1\Pi_u$ states is actually in error in TDDFT by ca. 1 eV at R_e, and even more at elongated bond length. We can trace the singularly large error in this case to inability of the linear response based TDDFT method to incorporate double excitation character.

The second application is to permanganate, MnO_4^-. The spectrum of this tetrahedral metaloxo-anion has been obtained with detailed vibrational structure in 1964. Since then virtually all quantum chemical methods have been benchmarked against this spectrum, but still the interpretation of the spectrum remains controversial. We will reproduce, using TDDFT with vibronic coupling, for the first time the full vibrational structure. This leads to a definitive assignment.

N_2: M. Grüning, O.V.Gritsenko, S.J.A. van Gisbergen and E.J. Baerends "Shape corrections to exchange-correlation Kohn-Sham potentials by gradient-regulated seamless connection of model potentials for inner and outer region", J. Chem Phys. **114** (2001) 652-660; J. Neugebauer, E.J. Baerends, "Vibronic coupling and double excitations in linear response time-dependent density functional calculations: dipole-allowed states of N_2", J. Chem. Phys. **121** (2004) 6155-6166.

MnO_4^-: J. Neugebauer, E.J. Baerends, M. Nooijen, "Vibronic structure of the permanganate absorption spectrum from time-dependent density functional calculations", J. Phys. Chem. A **109** (2005) 1168-1179

Non-adiabatic TDDFT MD: from gas phase to complex environments

Ivano Tavernelli

Lausanne, Switzerland

TDDFT calculations with the Gaussian augmented-plane wave approach

Juerg Hutter

Physical Chemistry Institute, University of Zurich

The Gaussian augmented plane wave (GAPW) approach combines the description of the Kohn-Sham orbitals as a linear combination of Gaussian functions with a mixed basis representation of the electron density. The density is separated in a smooth part, described in a plane wave basis and a rapidly varying part expanded in local Gaussian functions. This scheme leads to efficient algorithms for all-electron ground state Kohn-Sham calculations with periodic boundary conditions. We have further extended the GAPW method to include linear response TDDFT calculations. A series of approximations to the full equations (within the ALDA approach) was tested on molecular systems.

Calculation of optical properties of complex systems within TDDFT

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The microscopic study of complex systems has nowadays reached a high level of accuracy that allows for a deep understanding of the electronic excitations. Ab-initio descriptions of experiments such as direct or inverse photoemission, optical absorption, electron energy loss, have become possible thanks to the huge progress in theory and the increased computational power. Charged excitations, as well as neutral excitations, can now be studied within the Many-Body Perturbation Theory based on the Green's function formalism. Optical spectra can be calculated with inclusion of the electron hole interaction by solving the Bethe Salpeter equation (BSE) within the framework of Green's function theory.

Moreover, optical spectra can be nowadays also well described within the Time Dependent Density Functional Theory (TDDFT). The derivation of a long range exchange-correlation kernel suitable for optical spectra calculations will be briefly reviewed. Its performance, as well as those of simpler approximations, will be tested in the case of complex systems, like surfaces or liquids.

Practical aspects of molecular TDDFT calculations

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Universität Karlsruhe, Germany

Photochemistry has to date accumulated an immense amount of experimental data on molecular excitations and luminescence characteristics. Efficient implementations of TDDFT excited state Cartesian gradients [1,2] now provide computational tools for their interpretation and systematic investigation of excited state reactions. This is demonstrated for 7-azaindole dimer ((7-AI)$_2$) which is a very much investigated example for excited state intramolecular proton transfer. When excited to the S_1 state, (7-AI)$_2$ undergoes double proton transfer forming the tautomer [3]. Both concerted and stepwise mechanisms have been proposed for the double proton transfer, and the existence of an intermediate has been addressed in many experimental and theoretical studies.

TDDFT calculations using B3LYP functional and TZVPP basis reveal 3 excited state state minima in the S_1 state of (7-AI)$_2$. The excited state structures of normal dimer S_1^{N} and tautomer S_1^{T} show symmetry breaking which leads to full localization of the excitation on one monomeric unit. The third excited state structure corresponds to single proton transfer intermediate S_1^{I} and appears very low in energy due to strong charge transfer between the monomers. The mechanism of tautomerization has been investigated by 2-dimensional potential energy surface calculations along the proton transfer coordinates. The TDDFT results suggest that the tautomerization occurs by concerted yet not synchronous transfer of both protons, which is supported by recent experimental results [4]. The stepwise mechanism via S_1^{I}

intermediate seems to be rather a channel to fast radiationless relaxation to the ground state.

[1] F. Furche, R. Ahlrichs, J. Chem. Phys. **117**, 7433 (2002).
[2] J. Hutter, J. Chem. Phys. **118**, 3928 (2003).
[3] C. A. Taylor, M. A. El-Bayomi, M. Kasha, Proc. Natl. Acad. Sci. **69**, 253 (1969).
[4] K. Sakota, A. Hara, H. Sekiya, Phys. Chem. Chem. Phys. **6**, 32 (2004).

Exact-exchange spin-current density-functional theory

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A brief introduction of the optimized effective potential (OEP) method and exact-exchange Kohn-Sham approaches is given. Then a spin-current density-functional formalism that generalizes the current-spin-density- functional theory of Vignale and Rasolt is presented. The introduced spin-current density-functional theory (SCDFT) takes into account spin-currents, i.e., currents of the magnetization, in addition to the variables considered in current-spin-density-functional theory, i.e., the density, the spin-density, and currents of the density. An implementation of the presented SCDFT within an exact-exchange (OEP) framework is presented. The inclusion of relativistic effects, in particular of spin-orbit coupling, via relativistiv OEP pseudopotentials is discussed. Results for atoms and semiconductors are presented. It is shown that spin-orbit interactions are accompanied by spin-currents. Finally the perspectives of time-dependent SCDFT are briefly considered.

A. Görling, J. Chem. Phys. **123**, 062203 (2005) and references therein.
S. Rohra and A. Görling, Phys. Rev. Lett. **97**, 013005 (2006).
S. Rohra, E. Engel, and A. Görling, cond-mat/0608505.

The effect of nonlocality on the band gap within density functional theory

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and European Theoretical Spectroscopy Facility

In this talk I compare the eigenvalue band gap found with a nonlocal potential within the generalized KS (GKS)[1] scheme and within the KS scheme using the the optimized effective potential(OEP)[2] approach. Since I use the same exchange-correlation approximation (Coulomb-Hole screened-exchange) the difference in the band gap is due solely to the locality/nonlocality of the potential. In fact, I show that the difference between the OEP-KS and the GKS band gaps comes from the derivative discontinuity of the exchange-correlation energy that corresponds to the nonlocal potential. Once the derivative discontinuity is taken into account, the corrected KS and generalized KS gaps are very close to each other. Finally I discuss whether the GKS schemes can be successfully applied to calculations of optical absorption spectra of semiconductors and insulators.

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[1] A. Seidl et al. Phys. Rev. B **53**, 3764 (1996).
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Nonlocality and frequency dependence of effective potentials

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Many-body perturbation theory (MBPT) [1] is a very powerful method. The key variable is the Green's function $G(r, r', \omega)$ which contains a great deal of information, like the one-quasiparticle spectra. However, one is often interested in just a part of the information carried by G, so in these cases it is preferable to work with simpler quantities from the beginning. This is precisely the case of density-functional theory (DFT) [2], where one wants to obtain the ground-state total energy and density $\rho(r)$. In principle, one doesn't need the full G to obtain this information. In the Kohn-Sham approach [3] it is sufficient to solve an effective one-particle Schrödinger equation, with a local and static potential $V_{xc}(r)$. The Green's function, in turn, is determined by a nonlocal and frequency dependent self-energy $\Sigma(r, r', \omega)$. A possible link between DFT and MBPT is the Sham-Schlüter equation [4]:

$$V_{xc}(r_1) = \int d\omega dr_2 dr_3 dr_4 e^{i\eta\omega} \tilde{\chi}^{-1}(r_1, r_4) G_{KS}(r_4, r_2, \omega) \Sigma(r_2, r_3, \omega) G(r_3, r_4, \omega)$$

$$\tilde{\chi}(r_1, r_2) = \int d\omega e^{i\eta\omega} G_{KS}(r_1, r_2, \omega) G(r_2, r_1, \omega)$$

Here we generalize the Sham-Schlüter equation to situations where one is interested in other parts of the Green's function. For example, one can consider the trace of the spectral function, which is needed to interpret photoemission spectra. In this case a local and dynamical potential $V_{SF}(r,\omega)$ can be introduced. We show that in this case the nonlocality of the self-energy can be converted into a frequency dependence of VSF . This is illustrated for model systems. We discuss also the link with dynamical mean-field theory (DMFT) [5] and other approaches.

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Exchange-correlation functionals and kernels for conductance and polarisation

Rex Godby

York, UK

Transport in nanoscale systems: new approaches to an old problem

Massimiliano Di Ventra

San Diego, USA

Transport in nanoscale systems is usually described as an open-boundary scattering problem. This picture, however, says nothing about the dynamical onset of steady states, their microscopic nature, or their dependence on initial conditions.[1] In order to address these issues, I will first introduce a novel formulation of transport based on the physical notion of two large but finite charged electrodes discharging across a nanoscale junction. [1,2] This "microcanonical" picture suggests the description of electron flow by means of quantum hydrodynamic equations [3], allows us to prove that the total many-body current is given exactly in Time-Dependent DFT [1], and provides an elegant connection with Time-Dependent Current DFT [3]. As a bonus, we predict a series of novel phenomena like turbulence of the electron liquid [3], local electron heating in nanostructures [4] and the effect of electron viscosity on resistance [5]. We will provide both analytical results and numerical examples of first-principles electron dynamics in nanostructures using the above approach.

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Time dependent transport phenomena within TDDFT

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We propose a rigorous approach based on TDDFT to calculate total currents through and density in a molecule attached to macroscopically large reservoirs. We clarify under what circumstances a steady state can develop, discuss the initial-state and history dependences and obtain a Landauer-like formula for the steady current. We further show that the steady-state assumption is not compatible with the presence of bound states. The density oscillates with history-dependent amplitudes and, as a consequence, the effective potential of TDDFT oscillates too. A computationally tractable scheme of the theory is also presented. We develop a numerical algorithm based on the propagation of Kohn-Sham orbitals in open systems. The scheme is used to compute the time-dependent current in response to an external dc or ac bias or time dependent gate voltages (electron pumping). Finally, possible generalization of our approach are discussed.

Time-dependent generating-coordinate method

Carsten A. Ullrich

University of Missouri

The vast majority of applications in TDDFT use adiabatic approximations (such as the ALDA) for exchange and correlation. While the ALDA has overall been very successful, there are many situations where it fails. To go beyond the adiabatic approximation requires an xc potential with a memory, which is computationally demanding and has so far been achieved only in few exploratory calculations.

This talk presents a new, post-TDKS variational method which extends the ALDA in a flexible and computationally simple manner. The time-dependent many-body wave function is represented as a weighted sum of single-determinant, non-orthogonal wavefunctions coming from ALDA hamiltonians featuring a generating coordinate. The weight factors are obtained from a stationary action principle. As an illustration, the method is applied to describe driven parametric oscillations of two electrons in a harmonic potential (Hooke's atom). Comparison with exact solutions of the time-dependent two-electron Schroedinger equation shows that a proper choice of generating coordinates reproduces the linear and nonlinear electron dynamics very accurately, including effects associated with double excitations that cannot be captured with the ALDA alone.

Molecular dynamic simulations of non-adiabatic processes at surfaces

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Energy transfer processes at surfaces play an important role for various surface phenomena. During chemisorption, the binding energy of the adsorbate has to be dissipated into the substrate degrees of freedom. Concurrently with energy dissipation directly into phonons, part of the chemisorption energy can be spent to excite electron-hole pairs in the substrate. This electronic dissipation will be most pronounced for light adsorbate atoms interacting with metal surfaces, thus we focus on hydrogen atoms chemisorbing on an Al(111) surface. The electronic non-adiabacity has been demonstrated experimentally by H. Nienhaus [1] and coworkers by the direct observation of chemicurrents due to electron hole pairs induced by the chemical reaction. Here we investigate two different mechanisms that can contribute to the chemicurrents by simulating the chemisorption dynamics within TDDFT.

As a second example for energy transfer processes at surfaces we calculate the excitation of coherent surface-atom motion by very intense fs laser pulses. Such excitations are well known in case of bulk phonons, they still mark an active problem in case of atomic vibrations at the Si(001) surface.

TDDFT is ideally suited to simulate such electronically non-adiabatic processes *ab initio*. The adiabatic approximation is applied to the time-dependent exchange-correlation potential. The integration of the time-dependent Kohn-Sham equations has been implemented both into the original version of the total-energy program fhimd from the Fritz-Haber Institut in Berlin and into the program version by M. Bockstedte *et al.* extended for spin polarization. The calculations employ pseudopotentials, a plane-wave basis-set and periodically repeated supercells. For the situations considered here the dynamics of the ions is expected to be sufficiently accurately described within the Ehrenfest approximation. A time-dependent electric field perpendicular to the slabs can be used to simulate electron-hole pair-excitation by laser pulses.

Electron-hole pair excitation during H/Al(111) chemisorption has been simulated over up to 80 fs for cells containing up to 500 electrons. Due to computational limitations, the calculations had to be performed at a small plane-wave cut-off energy of 10 Ry and one special k-point. The dynamic of the electrons is analysed by a posteriori relaxation of the wave-functions down onto the Born-Oppenheimer surface at frozen-in atomic coordinates. In this way the energy stored in electron-hole pair-excitations, the non-adiabatic contribution to the force acting on the hydrogen atom, and the electronic excitation spectrum is calculated [2]. In this talk, the energy dissipation and the excitation spectra will be presented for H/Al(111), the isotope effect and kinetic energy dependence will be discussed, and the contribution to energy dissipation from the delocalisation of the local spin moment at the H-atom will be quantified and compared to the time-dependent Newns-Andersen model by Mizielinski *et al.* [3]

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Nonadiabatic functionals and their effects on electron dynamics in molecules and metal clusters

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Large Control of electronic currents by laser in quantum rings

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We show that the excited states of N-electron semiconductor quantum rings (QRs) can be controlled by a circularly polarized laser field [1]. For this purpose, we define a realistic 2D model potential for the QR and treat the influence of a tunable laser field on the electrons with the dipole approximation. In the numerical calculations we apply the time-dependent density-functional theory within the OCTOPUS code package [2], which enables the evolution of the electronic wave functions in real time and real space. This allows us to monitor the total density and current in the QR during the propagation. As a generalization to a recent study on one-dimensional QRs [3], we find that (i) an external magnetic field creating persistent currents does not affect the controllability of the excited states, and (ii) the finite width of the QR considerably changes the dipole matrix elements required for the determination of the pulse length. Finally we discuss the prominent role of the electron-electron interactions as well as the possibilities to fully control the many-electron system by using the framework of the optimal control theory.

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How do rewritable DVDs work: optical properties of phase-change materials

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Several chalcogenide alloys exhibit a pronounced contrast in the optical absorption of the metastable rocksalt and the amorphous state. This phenomenon is the basis for their application in the optical data storage.

Here I present ab initio calculations of the optical properties of GeTe and $Ge_1Sb_2Te_4$ in the rocksalt and the amorphous phase. These calculations reveal the correlation between local structural changes and optical properties as well as the origin of the optical contrast in these materials. We find that the change in the optical properties cannot be solely attributed to a smearing of the electronic states as commonly assumed for amorphous semiconductors: in fact the optical contrast between the two phases can only be explained by significant changes in the transition matrix elements.

Electronic excitations in hexagonal layered systems (C and BN)

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We present different phenomena involving electronic excitations in layered systems. For hexagonal boron nitride*, we show that excitonic effects play an important role for the optical properties. Measured and calculated values for the band-gap still display a strong scattering between 4.3 and 6.8 eV. We show that optical absorption and electron energy loss spectroscopy cannot be explained in terms of independent-electron transitions but can be properly understood only by proper inclusion of excitonic effects. We discuss the origin of the different values for the measured/calculated band-gaps. For the interpretation of Raman spectra of graphite, the double-resonant Raman model which involves electron-hole pair excitations is qualitatively successful. Quantitative evaluation based on DFT band-structures display, however, a mismatch between theory and experiments. We discuss the achievements and short-comings of the double-resonant model for the explanation of the differences in the Raman spectra of single-layer, few-layer, and bulk graphite.

* Collaboration with Andrea Marini and Angel Rubio (DIPC, San Sebastian, Spain)

** Collaboration with Davy Graf, Francoise Molitor, Klaus Ensslin, Christoph Stampfer, Alain Jungen, and Christopher Hierold (ETH Zurich, Switzerland)

The role of excitons in the optical properties of carbon nanotubes

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We present a first-principles study of the optical properties of single-walled carbon nanotubes (SWCNT). We employed many-body theoretical methods to determine the excited states of the system. Both self-energy corrections in the treatment of single-particle energies and effects arising from the electron-hole interaction are included in our calculations [1,2]. Our symmetry-based approach exploits all the symmetries of these systems, making feasible the study of large tubes with more than 200 atoms per unit cell, which are otherwise impossible to treat in standard approches within the many-body framework. In addition, this picture gives a more complete understanding of the excited state properties, of the degeneracies and group character of the single-particle bands, and of the selection rules involved in determining optical spectra. We computed one- and two-photon absorption spectra, achieving excellent agreement with recent experiments [3-5]. We found that many-electron effects are crucial in both the peak shapes and positions for all the tubes studied. In particular, for 0.4-0.8-nm-diameter tubes, the calculated exciton binding energies range between 0.3 and 0.9 eV, showing important excitonic effects even in large diameter nanotubes.

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TDDFT description of electronic systems in semiconductor heterostructures

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Turbocharging time-dependent density-functional theory with Lanczos chains

Stefano Baroni

Trieste, Italy

The large-scale application of TDDFT to nano-structured materials is currently hindered by our poor knowledge of the relevant exchange-correlation functionals in the dynamical regime, as well as by the lack of efficient algorithms applicable to systems larger than few (or few tens at the very best) independent atoms. In this talk a new algorithm will be described which allows for the application of TDDFT to systems of the same complexity as those currently treatable using state-of-the-art ground-state DFT techniques.

Using a super-operator formulation of linearized time-dependent density-functional theory, the dynamical polarizability of a system of interacting electrons is represented by a matrix continued fraction whose coefficients can be obtained from the non-symmetric block-Lanczos method. The resulting algorithm, which is particularly convenient when large basis sets are used, allows for the calculation of the full spectrum of a system with a computational workload only a few times larger than needed for static polarizabilities within time-independent density-functional perturbation theory. The method is demonstrated with calculations of the spectra of benzene and of fullerene, and prospects for its application to the large-scale calculation of optical spectra, particularly in what concerns the acceleration of the Lanczos recursion, are discussed.

TDDFT-MD simulation of nano-carbons: Decay dynamics of hot-carriers and electronic shakeup by high-speed ions/atoms

Yoshiyuki Miyamoto

Fundamental and Environmental Research Laboratories, NEC

In this talk, I will show applications of the TDDFT on molecular dynamics in nano-carbons. Since both electron dynamics and ionic motions are treated simultaneously, the TDDFT-MD simulation can treat both electron-electron interaction (within DFT) and electron-phonon interaction.
I show two examples of the applications: hot-carrier decay in carbon nanotubes and stopping power acting on high-speed hydrogen atom/ion passing through a graphene sheet.
The electronically excited carbon nanotubes are placed under particular lattice temperature, and time-evolution of expectation values of electrons and the potential energy of ions (the total energy) were monitored. We observed two-major time-domains of the electron-hole gap reduction which were respectively interpreted as electron-electron and electron-phonon interactions. This interpretation was further confirmed by monitoring a dependence of the decay dynamics on initial lattice temperatures.
Next example is high-energy hydrogen irradiation on a graphene sheet which shows significant reduction on the hydrogen kinetic energy even when kinetic energy transfer on carbon atoms in the graphene sheet is negligible. The reason of the significant stopping power is electronic shakeup which corresponds to collective excitation of valence electrons of graphene. This shakeup can be seen when the incident kinetic energy of hydrogen atom/ion exceeds 1 KeV. Meanwhile, the conventional Born-Oppenheimer approximation is found to be valid when the incident kinetic energy is less than 100 eV.
If time is allowed, I will discuss possible future applications of the TDDFT-MD simulation.

The present works have been done in collaboration with Profs. A. Rubio, D. Tománek, and Dr. A. Krasheninnikov. Part of the present calculations were performed by using the Earth Simulator.

The band gap of InN and ScN: a quasiparticle energy study based on exact-exchange density-functional theory

Patrick Rinke

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The group-IIIA nitride InN and the group-IIIB nitride ScN have recently received increased attention in the field of opto-electronics and optical coatings. Due to the difficulty of growing clean samples, however, the size of their band gap has not been well established, yet. We have recently shown, that quasiparticle energy calculations in the G_0W_0 approximation based on density-functional theory (DFT) calculations in the exact-exchange (EXX) approach yield band gaps in very good agreement with experiment for GaN and II-VI compounds [1]. For wurtzite InN our approach predicts a gap of 0.7 eV supporting recent experimental observations [2,3,4]. Extrapolating the G_0W_0 data to higher carrier concentrations, which are prevalent in most InN samples, results in an increase of the apparent band gap with increasing concentration (Burnstein-Moss effect) in good agreement with the observed blue shift of the optical absorption edge [4]. Moreover, the concentration dependence of the effective mass, which is a result of the non-parabolicity of the conduction band, agrees well with the experimental findings [4]. For ScN there exists a longstanding controversy if the material is a semimetal or semiconductor, which has only very recently been resolved in favor of the latter. Our calculations for rocksalt ScN predict an indirect band gap of 0.9 eV in good agreement with recent experimental observations [5].

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The role of core states in the excitation spectra of solids

Claudia Ambrosch-Draxl

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All-electron full-potential methods are highly precise and allow to explore the physics of the core region of solids, since no shape approximation is made for the potential when solving the Kohn-Sham equation. Thus they are reliable tools when heavy atoms are involved in a material, and they are also often used as a benchmark for other codes in terms of accuracy. But they are quite demanding regarding the computational effort and when it comes to the implementation of new features, particularily those related to excited states. Several discrepancies with respect to planewave calculations, which have been reported in literature, ask for clarification, and hence, for a wider range of applications. In this talk, the implementation of various methods into the full-potential linearized augmented planewave (LAPW) method is presented, comprising the exact exchange scheme (EXX), many-body perturbation theory (MBPT), as well as time-dependent density functional theory (TDDFT). Discrepancies with respect to planewave results – which show up in the EXX Kohn-Sham band gaps, the GW self-energies, as well as the electron-hole wavefunctions obtained by the Bethe-Salpeter Equation (BSE) – will be discussed, highlighting the importance of the core-valence interaction and the proper treatment of the wavefunctions close to the nucleus. Finally, first all-electron TDDFT spectra will be presented.

2.1.2 Report on IWOSMA-3

International Workshop on Orbital and Spin Magnetism of Actinides (IWOSMA-3)

Walter Temmerman
Daresbury United Kingdom

James Tobin
Lawrence Livermore National Laboratory United States

Gerrit van der Laan
Daresbury Laboratory United Kingdom

Timing
Number of days : 2
Start : 2006-06-01
end : 2006-06-02
Location of the activity
CECAM, 46 allée d'Italie, 69007 Lyon, France

Support

CECAM
Psi-k

Description

This International Workshop on Orbital and Spin Magnetism of Actinides (IWOSMA) is the third in a series. The first workshop took place in Daresbury in 1999 and the second in Berkeley, CA, USA in 2002. These workshops are informal gatherings of theoreticians and experimentalists addressing the latest issues in the electronic and magnetic properties of actinides.

Scientific Objectives

The magnetism of transition metal systems and lanthanide systems is now fairly well understood, where d and f electrons can be described in a delocalized and localized model, respectively. On the other hand, actinide systems do not fit in such a description. The localization of the 5f is in between that of the 3d and 4f and the strong spin-orbit interaction necessitates a relativistic approach. Furthermore, electron correlation effects play a major role in these compounds. Recently, it has become possible to determine element-specific magnetic moments using neutron diffraction and x-ray scattering and absorption. The latter technique makes it even possible to separate the orbital and spin contribution to the total magnetic moment. The results are very interesting but difficult to reproduce with present state-of-art calculations. Not only a very large orbital polarization but also a large magnetic dipole term has been measured in cubic compounds, such as US. This allows for severe testing of the extra terms included in band theory to account for orbital polarization. It is also clear that deeper insight in magnetism can be obtained by studying the unusual behaviour of the actinides. The recent development and application of such techniques as DMFT could contribute to the understanding of magnetism in actinides. Despite the fact that actinides for health reasons will find less application in technological market products, the understanding of their magnetic and electronic properties will no doubt provide key elements for a general description of electron correlation and relativistic effects.

Presentation List

How to calculate the critical temperature of superconductors

E.K.U. Gross
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Abstract

The traditional model of Bardeen, Cooper and Schrieffer (BCS) properly describes the universal features that all conventional superconductors have in common, but it is not able to make accurate predictions of materials specific properties such as the critical temperature. To tackle this problem, a novel density-functional approach is developed [1] which treats both the electron-phonon interaction and the electron-electron repulsion on the same footing. The formalism can be viewed as the superconducting generalization of the multi-component density-functional theory [2] for electrons and nuclei. Approximations of the universal xc functionals are derived on the basis of many-body perturbation theory [1,3]. In this way, a true ab-initio description is achieved which does not contain any empirical parameters. Numerical results for the critical temperature, the gap, the jump of the specific heat, and the exponent of the isotope effect will be presented for simple metals [4], for MgB_2 [5], and for Li, Al and K under pressure. In particular, for MgB_2, the two gaps and the specific heat as function of temperature are in very good agreement with experimental data. For Li and Al under pressure the calculations explain why these two metals behave very differently, leading to a strong enhancement of superconductivity for Li and to a clear suppression for Al with increasing pressure [6]. Finally, the peculiar properties of Pb are found to arise from two-gap superconductivity, somewhat similar to MgB_2.

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Orbital Ordering in actinide oxides: new perspectives on old problems

Gerry Lander
JRC-ITU, France

Abstract

The behaviour of the actinide oxides has been of major interest since the 1940s. UO_2 is known to order with antiferromagnetic order since neutron experiments of the 1960s. However, the puzzle of the lack of ordered magnetism in NpO_2 (also dating from the same period) was recently solved by the discovery [1,2] that the ordering phenomenon in NpO_2 is not connected with dipole moments (as in UO_2), but rather with the long-range ordering (at 25 K) of the anisotropic 5f charge distribution surrounding the Np^{4+} ion. Such ordering involves the 5f quadrupole charge distributions, and is commonly known as ”orbital ordering”. It cannot be observed with neutrons (or muons) but can be measured by resonant x-ray scattering. Following the work on pure NpO_2, we have re-examined single crystals of $(U_{0.75}Np_{0.25})O_2$ and shown that both the U and Np ions in this material exhibit dipole and quadrupole ordering [3]. All theoretical models of UO_2 emphasize the importance of the interplay between the Jahn-Teller and quadrupolar interactions, but direct evidence for such quadrupolar ordering was difficult to find in UO_2 as the quadrupolar interactions are weaker than the dominating dipole ones. We have now provided that evidence [4] and also shown definitively the triple-q nature of the magnetic ordering in UO_2. [5] This talk will review these experiments, some of the theories currently being advanced, and what remains to be done in understanding these complex actinide oxides at low temperature.

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Determining the Electronic Structure of Pu using Unorthodox Spectroscopies

James Tobin
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Abstract

The standard method to determine the band structure of a condensed phase material is to (1) obtain a single crystal with a well defined surface and i (2) map the bands with angle resolved photoelectron spectroscopy (occupied or valence bands) i and inverse photoelectron spectroscopy (unoccupied or conduction bands). i Unfortunately, in the case of Pu, the single crystals of Pu are either nonexistent, i very small and/or having poorly defined surfaces. i Furthermore, effects such as electron correlation and a large spin-orbit splitting in the 5f states i have further complicated the situation. i Thus, we have embarked upon the utilization of unorthodox electron spectroscopies, i to circumvent the problems caused by the absence of large single crystals of Pu with well-defined surfaces. i The talk will include a discussion of resonant photoelectron spectroscopy [1], i x-ray absorption spectroscopy [1,2,3,4], i electron energy loss spectroscopy [2,3,4], i Fano Effect measurements [5], i and bremstrahlung isochromat

spectroscopy [6], including the utilization of micro-focused beams to probe single-crystallite regions of polycrystalline Pu samples. [2,3,6] This work was performed under the auspices of the U.S. DOE by Univ. of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

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Electronic properties of Pu-Am

Ladia Havela
Prague, Czech Republic

Abstract

The specific position of Pu just at the localization threshold makes it very sensitive to external variables. Surprizingly, various allotropic phases have nearly identical weak magnetic susceptibility, i despite a large volume expansion exceeding 20% for the fcc delta-Pu comparing to monoclinic alpha-Pu. i This makes the scenario, in which the volume expansion is the way to formation of magnetic moments, rather questionable.

To resolve the issue whether an additional lattice expansion can lead to a 5f localization beyond the delta-Pu level and/or to onset of magnetism we focused on the Pu-Am system. The solid solution of Am in Pu stabilizes the fcc phase down to the lowest temperatures, expanding the volume. Available experimetal data indicate that the magnetic properties remain weakly paramagnetic up to at least 30% Am. Similarly, the gamma coefficient of the specific heat per Pu atom does not increase, and very little variations of the character of the 5f states are indicated by photoelectron spectroscopy.

The experimental findings can be understood on the basis of LSDA+U calculations of the Pu-Am system,

which reveal very little impact of varying the Am concentration and expanding the lattice on the Pu-5f states and their non-magnetic state.

Some aspects of the calculation of spin and orbital magnetization densities

Mike Brooks
Uppsala, Sweden

Abstract

The relationships between current, magnetic moment and magnetization densities are discussed. The approximations made in obtaining these densities from Ab initio energy band calculations are outlined. Particular emphasis is placed upon the interpretation of neutron diffraction experiments on intermetallics containing cerium or actinides with small magnetic moments, where the bonding electron density and spin density from the broad 5d or 6d bands becomes important. Since the bonding spin densities are absent in atomic calculations the entire interpretation of the experiments may be changed. Examples are $CeFe_2$ and UFe_2 where consistency between neutron diffraction and XMCD experiments is obtained.

Strong Correlations Across the Actinide Series:

Gabi Kotliar
Rutgers, United States

Abstract

The actinides realizations of many interesting many body physics phenomena such as the Mott transition, and provide the motivation for the developments of first principles methods to correlated materials.

In this talk we will discuss some of the lessons learned from applying realistic Dynamical Mean Field Theory to Plutonium and Americium and contrast the Mott transition in these two systems.

Calculation of Spectroscopic Properties of Actinide compounds

Hubert Ebert
Univ. München, Germany

Abstract

Electron spectroscopies are the most direct experimental tool to probe the electronic structure of a material. However, to allow for a one-to-one comparison with theory the calculation of corresponding spectra has to deal in an adequate way with all aspects of the electronic structure and also to account properly for the experimental situation. For actinide compounds this requires in particular an adequate treatment of relativistic as well as correlation effects. In our contribution we present a corresponding theoretical description of magnetic Compton scattering that is used to probe the spin magnetic properties. In a second study dynamical mean field theory (DMFT) is used to achieve at an improved description of the optical and magnetooptical properties of actinide compounds.

Spectral Density Functional Calculations in d and f electron systems

Sergej Savrasov
University of California, United States

Abstract

We will discuss spectral density functional method used to calculate total energies and one electron spectral functions of strongly correlated systems. The method employs dynamical mean field theory and exact diagonalization technique as a self-consistent algorithm to find redistribution of spectral weight originally deduced from density functional LDA band structures. As a result, a much wider class of systems showing phenomena such as Mott transition, atomic multiplets, Kondo effect, ordered and disordered atomic magnetism, etc can be explored. Aplications to Mott insulating oxides, actinides and heavy fermion superconductors will be dicussed and contrasted to experimental data and predictions of LDA band structures.

High Pressure Structural Phase Transformations in Curium, Americium and Americium Curium alloys

Rajeev Ahuja
University of Uppsala, Sweden

Abstract

Density-functional electronic structure calculations have been used to investigate the high pressure behavior of curium (Cm), americium (Am) and americium-curium alloys (AmCm). The phase transitions from fcc to the low symmetry structures are shown to originate from a drastic change in the nature of the electronic structure induced by the elevated pressure. For the low density phases, an orbital polarization correction to the local spin density(LSD) theory was applied. Gradient terms of the electron density were included in the calculation of the exchange/correlation energy and potential, according to the generalized gradient approximation (GGA). Theory compares rather well with our recent experimental data (Science 309, 110 (2005)). The new phase (Cm-III) phase is linked to magnetism.

Ab initio study of the electronic properties and Fermi surface

Sebastien Lebegue
LCM3B (UMR UHP -CNRS 7036), France

Abstract

The electronic structure of the uranium dipnictides UX_2 (X=As, Sb, and Bi) is investigated by means of it ab initio calculations based on density functional theory. The calculated Fermi surfaces are presented and compared to available experimental models obtained from de Haas-van Alphen experiments. In agreement with experiments they are found to have a significant two dimensional character. Also, the change of the electronic properties through the series is discussed.

References

S. Lebègue, P. M. Oppeneer, and O. Eriksson
Phys. Rev. B 73, 045119 (2006)

Localization of 5f Electrons and Phase Transitions in Americium

Michel Penicaud
CEA, France

Abstract

Density-functional electronic calculations have been used to investigate the high-pressure behavior of americium. The phase transitions calculated agree with the recent sequence obtained experimentally under pressure; double hexagonal close packed → face centered cubic → face centered orthorhombic → primitive orthorhombic. In the first three phases the 5f electrons are found localized, only in the fourth phase (Am IV) the 5f electrons are found delocalized. The localization of the 5f electrons is modeled by an anti-ferromagnetic configuration which has a lower energy than the ferromagnetic ones. In this study the complex crystal structures have been fully relaxed.

The microscopic 5f magnetisation of the superconductor PuCoGa5

Arno Hiess
ILL, France

Abstract

$PuCoGa_5$ is a superconductor with a critical temperature of T = 18 K and an upper critical field estimated to exceed Bc2 $\rangle$ 70 T; both parameters are records in this class of intermetallic strongly correlated electron systems [1]. The superconductivity is thought to be unconventional and carried by strongly correlated electrons involving the 5f electrons of plutonium [2]. No magnetic order has been observed in $PuCoGa_5$ down to T = 1 K, the lowest temperature measured. Those measurements suggest the bulk magnetic susceptibility to follow a modified Curie-Weiss behaviour in the normal state with an effective moment μ = 0.5 μ_B, and the induced magnetic moment at B = 10 T and T = 20 K had been proposed to correspond to about μ = 0.01 μ_B. To investigate the microscopic magnetic properties further and possibly to shed light on the relevance of the magnetism for the superconductivity, we here report on experiments using polarised neutron diffraction. This experimental technique is sensitive to periodically arranged magnetic moments only and allows determination of the Pu 5f form factor. The method is it insensitive to any magnetic contribution from random impurities or sample mount. The polarised neutron experiment has been performed on the hot neutron diffractomater D3 at the ILL i after determination of crystallographic parameters under similar experimental conditions by non-polarised neutron diffraction on D9. We used a large single crystal (2 * 2 * 4 mm^3 grown from 242Pu. We discovered that the induced magnetic moment is even smaller than previously reported. New bulk susceptibility measurements performed on the same single crystal are consistent with the neutron investigations. This result challenges the currently discussed models for the superconductivity in this weakly magnetic compound.

References

[1] J. L. Sarrao et al., Nature 420, 297 (2002)
[2] N. J. Curro et al., Nature 434, 622 (2005)

Lattice dynamics of light actinides

Johann Bouchet

CEA-DIF, France

Calculated de Haas-van Alphen frequencies of NpCoGa5

Ingo Opahle

IFW Dresden, Germany

Abstract

The electronic structure and magnetic properties of NpCoGa$_5$ are investigated in the framework of relativistic density functional theory in the local spin density approximation (LSDA) with and without orbital polarization (OP) corrections. A detailed analysis of the Fermi surface is presented. Comparison of the calculated angular dependence of the de Haas-van Alphen frequencies with recent experimental data shows that LSDA reproduces the main features of the Fermi surface topology, while the spin and orbital moments of NpCoGa$_5$ are less well described. The inclusion of OP corrections leads to a very good agreement between calculated and measured de Haas-van Alphen frequencies, but does not yield a significant improvement of the calculated magnetic properties. We predict that NpCoGa$_5$ shows an intrinsic GMR effect at moderate magnetic field.

References

I. Opahle, S. Elgazzar, V. D. P. Servedio, Manuel Richter, and
P. M. Oppeneer, Europhys. Lett. 74 (2006) 124.

Excess Magnetic Susceptibility Arising From Self Damage in Pu and Pu Alloys

Scott McCall

LLNL, United States

Abstract

The 5f-electrons of both α-Pu and δ-Pu occupy a narrow f-band as indicated by both the magnitude of the electronic specific heat and the large Pauli magnetic susceptibility ($\sim$ 500 μemu/mol Pu), with no indication of local magnetic moments in the "pure" metal. Pu decays by emission of a 5 MeV alpha particle and corresponding 86 keV U recoil, generating a damage cascade of $\sim$2500 vacancies and interstitials. Most of these immediately recombine, but a few hundred defects remain, and at low temperatures (T$\langle$ 35K), they become frozen within the lattice. This damage is observable as an increase in the magnetic susceptibility with time (damage) that returns to the undamaged initial (t=0) value after annealing to 350K. Thus the excess magnetic susceptibility (EMS) arises from the defects, and not the decay products which are unaffected by thermal annealing. The EMS is well described by a two component function: χ_ν(1-exp(-t/τ))+χ_D't, where both χ_ν and χ_D' are functions of temperature, while the characteristic time, τ, is temperature independent with $\tau_\alpha \rangle \tau_\delta$. These characteristic times are inversely proportional to a volume of magnetic influence arising from the damage cascades that is significantly

larger than the region of physical damage predicted by simulations. The temperature dependence of χ_ν obeys a Curie-Weiss law which suggests there are evolving localized magnetic moments and hinting at characteristics of the 5f electrons hidden in the undamaged material. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Probing the magnetism of acinides with μSR techniques

Alain Yaouanc

CEA/DSM, Departement de Recherche Fondamentale sur la Matiere Condensee F-38054 Grenoble Cedex 9, France, France

Abstract

As the nuclear magnetic resonance (NMR) techniques, the positive muon spin rotation and relaxation (μSR) techniques provide information on the static and dynamical properties of the magnetic field at the probe site. Taking examples from the published literature, we shall illustrate the possibilities offered by these techniques.

One of their key characteristics is their ability to detect magnetic moments which may not be dipole-like. NpO_2 offers a typical example. One may observe magnetic reflections in diffraction techniques while no magnetic moments are detected by μSR because of their relatively fast fluctuation rate. UPt_3 is an example. In contrast to NMR, measurements can be carried out in truely zero field. This allows to detect quasi-static small itinerant magnetic moments as in UGe_2. Finally, we shall discuss the investigation of the superconductivity of materials, in particular the symmetry and the temperature dependence of the London penetration depth.

Magnetic Susceptibility of $PuCoGa_5$ from ITU-SQUID measurements

Franck Wastin

Karlsruhe, Germany

Abstract

Magnetism and unconventional superconductivity are interdependent in strongly correlated electron systems. $PuCoGa_5$ displays superconducting behavior, with a critical temperature of Tc = 18.5 K and an upper critical field Bc2(0) estimated to exceed 70 T [1], considered to be unconventional and carried by strongly correlated 5f electrons [2]. No magnetic order has been observed down to T = 1 K but the temperature dependence of the magnetic susceptibility of $PuCoGa_5$ is indicative of local-moment behavior close to that expected for Pu^{3+}. Initial bulk measurements on a single crystal were reported to follow a modified Curie-Weiss behavior in the normal state with an effective moment μ_{eff} = 0.68 μ_B, and an induced magnetic moment at B = 1 T and T = 20 K corresponding to about 5.55 mμ_B. However, further unpublished experiments on various single and polycrystalline samples led to a large discrepancy in the induced moment measured. In this work, we present the efforts conducted at ITU to distinguish the intrinsic magnetic susceptibility of $PuCoGa_5$.

References

[1] J. L. Sarrao et al., Nature 420, 297 (2002)

[2] N. J. Curro et al., Nature 434, 622 (2005)

X-ray Magnetic Circular Dichroism study of U/Fe multilayers

Fabrice Wilhelm

ESRF, France

Abstract

X-ray magnetic circular dichroism (XMCD) measurements have been performed at the U M4,5-edges and Fe K-edge on well-defined uranium/iron multilayers with different compositions. i The multilayers have layer thicknesses in the range 9 to 40 A for uranium and 9 to 34 A for iron. i Temperature and element-specific magnetic hysteresis curves show that the easy magnetization axis lies in-plane. i At both 10 K and room temperature, the U layers have been found to be magnetically polarized in all of the multilayers studied. An induced U magnetic moment (maximum value $\sim$ 0.1 μ_B, coupled parallel to the Fe magnetic layers through the exchange coupling, has been observed and is mainly located at the interfaces. The value of the orbital to spin ratio for the induced U moments is $\sim$ 2.1, suggesting moderate hybridization between the U 5f and Fe 3d states.

Theory of Am and Pu systems.

Axel Svane

Aarhus, Denmark

Abstract

Two aspects of the theory of electronic structure of actinides are addressed. Equilibrium lattice constants and effective valencies are calculated on the basis of the self-interaction corrected local spin density total energy functional. We consider the actinide elements Pu, Am, Cm and Bk, as well as alloys of Pu and Am. Secondly, the spectral function of well localized actinide systems is evaluated on the basis of the multiplet Hubbard-I approach, where an additional interaction is introduced to represent fluctuations of the f-shell configuration. The approach is applied to Am and PuSe, and gives good agreement with photoemission data.

Program

Day 1: June 01 2006

Session : 1 Experimental Aspects

09:30 to 10:15 : Presentation

Orbital Ordering in actinide oxides: new perspectives on old problems
Gerry Lander

10:15 to 11:00 : Presentation
Determining the Electronic Structure of Pu using Unorthodox Spectroscopies
James Tobin

11:00 to 11:30 : Coffee Break

11:30 to 11:55 : Presentation

11:55 to 12:20 : Presentation
Magnetic Susceptibility of PuCoGa5 from ITU-SQUID measurements
Franck Wastin

12:20 to 14:00 : Lunch Break

Session : 2 Theoretical Aspects
14:00 to 14:40 : Presentation
Some aspects of the calculation of spin and orbital magnetization densities
Mike Brooks

14:40 to 15:20 : Presentation
Theory of Am and Pu systems.
Axel Svane

15:20 to 16:00 : Presentation
Spectral Density Functional Calculations in d and f electron systems
Sergej Savrasov

16:00 to 16:30 : Coffee Break

16:30 to 17:00 : Presentation
Calculation of Spectroscopic Properties of Actinide compounds
Hubert Ebert

Day 2: June 02 2006

Session : 3
09:00 to 09:40 : Presentation

Strong Correlations Across the Actinide Series:
Gabi Kotliar

09:40 to 10:05 : Presentation
Excess Magnetic Susceptibility Arising From Self Damage in Pu and Pu Alloys
Scott McCall

10:05 to 10:30 : Presentation
High Pressure Structural Phase Transformations in Curium, Americium and Americium Curium alloys
Rajeev Ahuja

10:30 to 11:00 : Coffee Break

11:00 to 11:15 : Presentation
Ab initio study of the electronic properties and Fermi surface
Sebastien Lebegue

11:15 to 11:40 : Presentation
Electronic properties of Pu-Am
Ladia Havela

11:40 to 12:05 : Presentation
Localization of 5f Electrons and Phase Transitions in Americium
Michel Penicaud

12:05 to 12:30 : Presentation
X-ray dichroism studies of the crystalline and magnetic properties of UFe2
Andrei Rogalev

12:30 to 14:25 : Lunch Break

Session : 4
14:25 to 14:50 : Presentation
The microscopic 5f magnetisation of the superconductor PuCoGa5
Arno Hiess

14:50 to 15:15 : Presentation
How to calculate the critical temperature of superconductors
E.K.U. Gross

15:15 to 15:30 : Presentation
Lattice dynamics of light actinides

Johann Bouchet

15:30 to 16:00 : Coffee Break

16:00 to 16:15 : Presentation
X-ray Magnetic Circular Dichroism study of U/Fe multilayers
Fabrice Wilhelm

16:15 to 16:40 : Presentation
Calculated de Haas-van Alphen frequencies of NpCoGa5
Ingo Opahle

Organizer's report

Conclusions

1. Great meeting.

2. Exciting science.

3. Expanding field.

4. Are we starting to understand the electronic structure of Pu and other actinides ? The valence electronic structures of the actinide metals and alloys in general and plutonium (Pu) in particular remain mired in controversy. Interestingly, the various phases of Pu metal provide a microcosm of the metallic actinides as a whole. Thus, unravelling the nuances of the interplay of electronic and geometric structures in Pu will illuminate the properties of all transuranic metals. In a sense, the behavior of the Pu 5f electrons is completely counter-intuitive. The dense phase, alpha, has some semblance of delocalization in the 5f valence bands and can be treated theoretically within single electron models such as the Local Density Approximation. The alpha phase is monoclinic, which is a low symmetry ordering. The less dense delta-phase is fcc and exhibits evidence of localized and/or correlated electronic behavior. The fcc is a high symmetry phase which is normally associated with superior wavefunction overlap in d state metals. But herein is the key: the linear combinations of the 5f's do not produce the nicely lobed wavefunctions with symmetry about the x, y, z and diagonal axes, as occurs for d states. Instead, the linear combinations of f -states have oddly lobed and badly directed wavefunctions which match very poorly with the high symmetry of the fcc structure. In the rare earths and lanthanides, this odd lobing is of no consequence: generally, the 4f valence states are inside the outer 5d, 6p and 6s electrons and can be treated as isolated, atomic-like orbitals that do not participate in chemical bonding. In the actinides, the 5f's are less well shielded. Shielding is undoubtedly a key issue and relates to the volume changes. In fact, the 20% volume increase of Pu between the alpha and delta phases is a reflection of the discontinuous 30% volume jump between Pu and Am, as one moves along the row of actinide elements. Furthermore, the fcc delta- Pu can not be treated theoretically without ad hoc corrections, e.g., the addition of Coulombic repulsion terms to LDA formalisms. Finally, we have not even begun to deal with the issue of dilute alloy formation and its impact upon the electronic structure of metallic actinides. The

upshot of this is that the valence electronic structure of Pu in particular and the actinides in general is only poorly understood.

5. There are still a lot of challenges ahead

Recommendations

1. Let’s meet again: IWOSMA-4 is planned to be held in Prague and to be organized by Ladia Havela.
2. Do more experiments on actinides.
3. Work on clean samples.
4. Use a multi-technique approach and explore core-hole spectroscopy.
5. Do more calculations for these systems taking their correlated nature into account.

Participant List

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2.2 ESF Psi-k Programme Workshop/Conference Announcements

2.2.1 Joint MolSimu-Psi-k Tutorial "Quantum Simulation of Liquids and Solids" within the CECAM MC Tutorial Series

Oct. 30 2006 to Nov. 10 2006
CECAM 46 allée d'Italie, 69007 Lyon, France

Organizers:

Evert Jan Meijer (University of Amsterdam, Netherlands)
Rodolphe Vuilleumier (Universitet Pierre et Marie Curie, France)
Igor Abrikosov (Linkoping University, Sweden)
Sergei Simak (Linkoping University, Sweden)

Description

This course is aimed at giving an introduction in the simulation of electronic structure in condensed phase materials, solids and liquids. A first series of lectures will be devoted to the basics of Density Functional Theory and to the solution of the electronic structure problem in solids using plane wave basis sets and Green's function technique. This part of the tutorial was based on the book by R. M. Martin "Electronic Structure. Basic Theory and Practical Methods" (Cambridge University Press, Cambridge, 2004). A second series of lectures will then focus on the simulation of liquid systems using ab initio Molecular Dynamics. These will also include an introduction to advanced techniques including simulation of reactive processes in liquids and coupling of quantum and classical simulations (so-called QM/MM).

The morning sessions are lectures introducing the methods and in the afternoons there are computer exercises in which these methods will be applied. During these practical classes the students will run a few simulations using existing packages, like CPMD, KKR-ASA and VASP, to apply the techniques discussed in the morning lectures and be acquainted with these packages. They will also write a simple program to solve a one dimensional Schrodinger equation with a periodic potential using a plane wave basis set. In addition, a miniworkshop will be organized, where participants can present results of their research.

The course does not assume any previous knowledge in molecular simulations. However, elementary knowledge in quantum and statistical physics is assumed.

Support for participation (travel and lodging) is available via the Marie Curie Action "MolSimu".

Register for the tutorial at

`http://www.cecam.fr/index.php?content=activities/`
`tutorial&action=details&wid=125`

Registration Deadline : Sep. 30, 2006.

3 Psi-k Training

3.1 Uppsala Graduate School in modern electronic structure theory, for chemists and physicists

December 11-18, 2006
Ångström laboratory, Uppsala, Sweden

Background and general information

The Uppsala graduate school on Modern electronic structure theory, for chemists and physicists is intended to give a basic background in electronic structure theory, and how it can be used to calculate materials properties with general applications in solid state physics and chemistry. These properties involve phase stability, structural properties, optical properties, magnetism, and correlated electron behaviour. The school will be held at the Ångström laboratory, Uppsala University in December 2006. The teaching will be done as a mixture of regular lectures combined with tutorials, and will be given by world leading experts in the field. The tutorials involve learning the fundamental and practical aspects of electronic structure methods such as the exact muffin-tin orbital method (EMTO), the linear combination of atomic orbital method (LCAO) and the LDA+U method as implemented in the linear combination of plane wave method (LAPW). The school will present either regular lectures or tutorial and each day will end with a 2-hour session where all teachers of the school are available for the studentsÕ questions and to participate in informal discussions. Lecturers that have accepted to teach are: Dr. R. Ahuja, Uppsala University, Sweden, Dr. A. Delin, Royal Institute of Technology, Stockholm, Sweden, Prof. M. Katsnelson, Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, The Netherlands, Prof. P. Mohn, Center for Computational Materials Science, Vienna, Austria, Prof. M. Richter, IFW Dresden, Germany, Dr. A. Shick, Institute of Physics, ASCR, Prague , Czech Republic and Dr. L. Vitos, Royal Institute of Technology, Stockholm, Sweden. Expected background for the course involves: quantum physics, atom and molecular physics and solid state physics. The Nobel prize lectures will be given in Uppsala during this week and a break in the programme will be made to enable the school attendants to listen to these lectures.

Registration, Conference fee and scholarships

The conference fee is 250 Euro. A limited number of scholarships will be available for young researchers to cover travel, hotel and living expenses. Registration is done via email to

Biplab.Sanyal@fysik.uu.se.

Deadline for the registration is November 30, 2006.

Schedule

Electronic structure methods, background and applications

Dec. 11 Introduction to density functional theory, Hartree-Fock theory of the uniform electron gas, the local density approximation and gradient methods. Introduction to solving the Kohn-Sham equation for solids and the total energy expression.
Lecturer: A. Delin (4 lecture hours)

Dec. 12 Introduction to magnetism, Stoner theory, localised versus band magnetism, Heisenberg model, Hubbard model, origin of the Weiss field, collective excitations, ordering temperature, mechanism for exchange interaction and different types of ordering.
Lecturer: P. Mohn (4 lecture hours)

Dec. 13 Introduction to light interacting with solids, the Kubo formalism, optical conductivity, Kramers-Kronig equation, magneto optic effects, calculations of optical properties of materials.
Lecturer: P. Oppeneer (2 lecture hours)

Dec. 13 Introduction to crystallographic phase stability and structural stability. Calculations of materials stability and elastic response. Evaluation of phase diagrams and pressure induced structural phase transitions. Applications to materials used in technology.
Lecturer: R. Ahuja (2 lecture hours)

Electronic structure methods, methodology:

Dec. 14 The LCAO method, including background and details of the method. Tutorial involving the use of the LCAO programme, involving calculations of e.g. equilibrium volume of bcc Fe, and the spin moment of fcc Ni.
Lecturer: M. Richter (2 lecture hours, 4 tutorial hours)

Dec. 15 The EMTO method, including background and details of the method. Tutorial involving the use of the EMTO programme, involving calculations of e.g. phase stability of Ni-Pt alloys.
Lecturer: L. Vitos (2 lecture hours, 4 tutorial hours)

How to choose effective potentials, what to use for which material ?

Dec. 18 Background to correlation phenomena.
Lecturer: M.Katsnelson (2 lecture hours)

Dec. 18 The LDA+U method in the LAPW formalism. Basic equations, double counting and practical implementation. Tutorial involves how to use the LDA+U/LAPW method with applications for transition metal oxides and f-electron systems.
Lecturer: A.Shick (2 lecture hours, 4 tutorial hours)

3.2 Bristol-Daresbury Graduate School

University of Bristol, United Kingdom

25-31 March, 2007 (One week duration)

A combined theory-hands-on Graduate School on the basics of electronic structure methods and calculations will take place in Bristol on March 25-31, 2007. The level is for graduate students just starting their Ph. D. course. There will be 20 lectures over 6 days, 10 lectures on theory and 10 lectures on electronic structure methods. The rest will be dedicated to hands-on exercises. Of the 10 lectures on theory there will be 5 on density functional theory (DFT) (including time-dependent (TD)-DFT), 3 on many-body theory (MBT) and 2 on dynamical mean field theory (DMFT). Of the 10 lectures on methods a bird's eye view will be given on 5 methods: PW, FPLO, LAPW, LMTO and KKR, each introduced in two lectures.

Further information will be posted on the Psi-k Training web pages:

http://www.mc-psi-k-training.cecam.org/

Informal queries can be e-mailed to w.m.temmerman@dl.ac.uk.

3.3 Summer School: Ab-initio Many-Body Theory

Organisers

A. Rubio, A. Lichtenstein, C. Filippi, A. Georges, and W. M. Temmerman

22-29 July 2007 (one week)

Palacio Magdalena, San Sebastian, Spain

The School is part of the summer courses of the University of the Basque Country

(http://www.sc.ehu.es/scrwwwsu/index.htm)

Summary

The School is a shared activity of the three working groups, WG1 (GW method), WG2 (quantum Monte Carlo) and WG3 (dynamical mean field theory). It aims at giving a unified overview of the three many-body approaches.

The School is the first Summer School in the Psi-k Marie Curie Series of Events (Psi-k Training in Computational Nanoscience). These Schools are complementary to the Hands-on tutorials offered within the same Programme and aim at providing understanding of the physical phenomena and materials in addition to the computational techinques which are then covered in the hands-on tutorials.

The School will reach out to young researchers already working in the general field of many-body ab-initio theory, as well as researchers who are not yet practitioners but are interested in acquiring the necessary expertise. The School will give a solid introduction to the description of electronic correlation effects on an ab-initio basis in both weakly and strongly correlated materials. It will provide the necessary background and context, highlighting the most challenging problems, and the topics of current interest. Finally, the program will try to achieve a good balance between theoretical and experimental lectures.

Proposed Program

The program will consist of 6 hours of lectures per day. Ample time will be given to informal discussions and interaction between students and teachers, including round tables addressing questions by the participants as well as highlighting new frontiers in the field.

Recognition of the course

We will use the European Credit Transfer system to express the work load of a given training activity: One European Credit (EC) corresponds to a work load of 25-30 hours including preparation. Therefore, a certificate will be given to all PhD and master students that have successfully participated in one of the training activities. The total ECTs for the present activity is of 2.

Participants

The call for participation will be mainly directed to students and scientists specialized on computational physics and quantum chemistry. We will limit the number of participants to 70, in order to ensure a maximum interaction between all the participants and the lectures.

4 General Workshop/Conference Announcements

4.1 AMN-3 Conference on Advanced Materials and Nanotechnology

11-16 February 2007

Wellington, New Zealand

http://www.macdiarmid.ac.nz/amn3/

The AMN-3 Conference on Advanced Materials and Nanotechnology (http://www.macdiarmid.ac.nz/amn3/) will be held 11-16 February 2007 in Wellington, New Zealand. Building on the hugely successful AMN-1 (2003) and AMN-2 (2005) conferences we intend to offer you a smorgasbord of the latest findings in the areas of nanotechnology and advanced materials.

Maintaining our programme

(http://www.macdiarmid.ac.nz/amn3/Programme/programme.html)

format, we will have two and a half days of plenary addresses from many of the best international and local researchers in these areas including
Prof Sir John Pendry (http://www3.imperial.ac.uk/people/j.pendry) ,
and Nobel Laureates Prof Stephen Chu (http://www.lbl.gov/Publications/Director/)
and Prof Sir Harry Kroto (http://www.sussex.ac.uk/chemistry/profile1523.html),
followed by two days of more highly specialised parallel sessions, including the fabulously successful breakfast poster sessions.

Topics covered include:

Advanced composite materials
Advanced materials characterization
Biomolecular assembly
Clusters, nano particles and quantum dots
Conducting polymers
Functionalised surfaces
Materials Modelling
Molecular electronics and nanoscience
Nanoengineering of materials and devices
Nano and microfluidics
Bio-nanotechnology
Nanolithography
Nanoscale and sub-wavelength optics
Nanotechnologies for energy
Nanotube growth and devices

Novel semiconductor materials
Optical and electronic materials
Quantum devices for information processing
Soft matter and complex fluids
Spintronics
Superconducting materials and devices

Abstract Submission Deadline was 31 August, 2006.

Early registration ends 3 November. To qualify you must be registered and paid by 3 November 2006.

Shaun Hendy
Industrial Research Ltd
PO Box 31-310
Lower Hutt
New Zealand
Ph 64 4 931 3248
Fax 64 4 931 3003

4.2 2nd Annual CNF Fall Workshop: *Building Nanostructures Bit by Bit*

Cornell Nanoscale Science and Technology Facility, Ithaca, NY

October 23th-25th, 2006

Organized by the NNIN/C (`http://www.nnin.org/nnin_compsim.html`)

Sponsored by the National Science Foundation

Workshop Coordinator: Derek Stewart (stewart@cnf.cornell.edu)

`http://www.cnf.cornell.edu/cnf_fallworkshop2006.html`

Overview: The nanoscale regime provides an important arena where scientific disciplines converge to study systems that can have tremendous fundamental and commercial impact. Modeling and simulation techniques play a crucial role in guiding nanoscale research and interpreting data. However, in order to successfully integrate these computational approaches with experimental tools, researchers must learn about the principles and applications associated with each code.

Format: This workshop will provide morning lectures on the theory behind different approaches followed by *hands-on* sessions on each code. In some cases, the participants will be able to learn directly from the code's creator. Graduate students and young researchers with theory or experimental backgrounds are encouraged to attend. More seasoned members of the field are also encouraged to come and share their knowledge.

Invited Speakers:
Dr. Steven Johnson (MIT) - nanphotonics MEEP and MPB
Dr. Axel Kohlmeyer (University of Pennsylvania) - Carr-Parrinello Molecular Dynamics (CPMD) and Quantum Espresso plane wave dft code
Dr. Nicola Marzari (MIT) - Carr-Parrinello Molecular Dynamics and Quantum Espresso
Dr. Steve Plimpton (Sandia National Laboratories) - LAMMPS molecular dynamics
Dr. Murilo Tiago (University of Texas) - PARSEC real space dft code

Important Dates: *Deadlines Extended!*
Poster Abstract Deadline: October 11th, 2006
Registration deadline: **October 11th, 2006**
Seating is limited to 30-40 participants. Please register early!

5 General Job Announcements

Post-doctoral Scientist

University of Notre Dame, USA

The Schneider group at the University of Notre Dame (http://www.nd.edu/) has an opening for a post-doctoral scientist to contribute to a recently funded DOE project in supported metal nanocatalysis. The candidate will have primary responsibility for applying first-principles DFT tools to simulate the structures, compositions, and reactivities of supported metal clusters as a function of external chemical environment, including the opportunity to contribute to the development of stochastic approaches to cluster optimization. The post-doctoral appointment will be for an initial period of two years, and will be at a competitive salary. More information about our on-going research in Computational Environmental Catalysis, including pointers to recent publications, is available at

`http://www.nd.edu/~wschnei1`.

Interested candidates should submit a CV and three references to Prof. Bill Schneider, University of Notre Dame, wschneider@nd.edu, (574) 631-8754.

Postdoctoral Position

Theoretical & Computational Condensed Matter & Materials Physics
University of South Florida, Tampa

Applications are invited for postdoctoral position in theoretical & computational condensed matter & materials physics. The work will involve research on large-scale atomistic simulations of matter at extreme conditions using molecular dynamics simulations, tight-binding and first-principles density functional theory.

The successful candidate must have a Ph.D. in theoretical or computational physics, chemistry, materials science or closely related fields. He/she must have demonstrated the ability to develop new theoretical methods, and implement these methods in computer programs. The candidate should have a substantial experience with density functional theory, tight-binding, molecular dynamics and other atomistic simulation techniques. Strong programming skills, knowledge of Unix/Linux computer environment as well as parallel programming using MPI are preferred.

The position is available immediately. The appointment is initially for one year, with the possibility of renewal up to three years. Applicants should send a curriculum vitae including list of publications, a statement of research experience, and list of 3 references to Prof. Ivan Oleynik at oleynik(at)shell.cas.usf.edu.

Graduate studentships are also available.

Ph. D. and Post-doctoral Positions

Department of "Computational Materials Design"

Max-Planck-Institut für Eisenforschung Düsseldorf, Germany

A Ph. D. and a Post-doctoral postions are now open at the department "Computational Materials Design" (Prof. Dr. J. Neugebauer) of the Max- Planck-Institut fuer Eisenforschung Duesseldorf, Germany. The positions are in the research group "Theory of Phase Transitions" (Dr. T. Hickel), which is focussed on the development and application of efficient simulation tools based on DFT and thermodynamics/kinetics in order to investigate martensitic phase transitions.

The aim of the projects is the theoretical investigation of:

– martensitic phase transitions, magnetic-field induced switching and motion of twin boundaries in novel shape memory alloys (priority program 1239 within the German Research Foundation),

– elastic properties of advanced high strength and supra-ductile steels, stacking faults and the impact of hydrogen.

We encourage outstanding and highly motivated candidates interested in fundamental materials research and open for intensive collaborations with industrial research instituts to apply. A strong background in theoretical solid states physics and quantum mechanics is required. The knowledge of electronic structure methods and computational tools including quantum chemistry will be considered as an advantage.

Applications are accepted until the position will be filled. The Max- Planck-Institut für Eisenforschung is an equal-opportunity employer.

Candidates are invited to send their CV, recent publications and contact data of two potential referees to

Dr. Tilmann Hickel
(t.hickel@mpie.de)

Ph. D. Position (BAT-O IIa/2)

Institute for Theoretical Physics

TU Bergakademie Freiberg, Germany

A Ph. D. position (BAT-O IIa/2) is immediately available at the Institute for Theoretical Physics at the TU Bergakademie Freiberg (Germany) to perform density-functional theory calculations and first-principles molecular dynamics simulations to investigate the system Si–Al–O–N at extreme pressures. The theoretical studies will be carried out in close collaboration with experimentalist in order to support and guide the search for novel materials. The position is granted for initial 2 years with the possibility to extend for 1 year. The research work will be performed under the direction of Prof. Jens Kortus within a DFG funded project in the German priority program 1236.

Candidates are expected to possess a solid background in materials science, physics, chemistry or engineering. Existing expertise in atomistic modelling of materials, DFT-based simulations or solid state physics represents an advantage. Knowledge of the German language is not required.

Interested candidates should send their application including CV and academic record to

Jens Kortus (Jens.Kortus@physik.tu-freiberg.de)
TU Bergakademie Freiberg
Theoretische Physik
Leipziger Str. 23
09599 Freiberg, Germany.

Review of applications will begin immediately and will continue until a suitable candidate is found.

Post-doctoral Position

Institute of High Performance Computing (IHPC)

Nanyang Technological University (NTU), Singapore

Currently we are seeking outstanding applicants for one postdoctoral position to be jointly appointed at Institute of High Performance Computing (IHPC), which could start immediately. We have our own high performance computing Rock cluster with 62 processors, besides access to computing resource at IHPC.

Candidates should have a Ph. D. degree in physics, chemistry, materials science or related disciplines, with strong experience in first principle computation and molecular dynamics simulation. The codes development work will be partly in collaboraiton with teams in USA. Salary is commensurate with demonstrated capabilities and experience. NTU offers an attractive and comfortable living environment.

Interested candidates should send their application including CV and academic record to

Dr. Haibin Su (hbsu@ntu.edu.sg)
Assistant Professor
Divison of Materials Science
Nanyang Technological University
50 Nanyang Avenue
Singapore 639798
Telephone: (65) 6790-4346
Fax: (65) 6790-9081

Review of applications will begin immediately and will continue until a suitable candidate is found.

Postdoctoral or Research Associate Position

National Renewable Energy Laboratory (NREL)

Solid State Theory Group: Theory of Nanostructures

http://www.sst.nrel.gov

NREL's Solid State Theory Group is looking to fill a Postdoctoral or a Research Associate position (depending on qualifications). The research area is on the theory of nanostructures. The position is available immediately and renewable upon mutual consent for up to 3 years. The salary range is $48,000 - $62,000 per year, depending on seniority, qualification and experience. Applicants are expected to have a strong background in solid-state theory and preferably in the area of nanostructures. For more details about ongoing work, see

http://www.sst.nrel.gov,

or contact directly Gabriel Bester.

The Solid State Theory Group is headed by Alex Zunger and 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 their curriculum vitae, list of publications (including preprints of unpublished papers, if possible), and arrange for two to three references addressed to:

Dr. Gabriel Bester, 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

`gabriel_bester@nrel.gov`.

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

Three Tenure-track Positions,

RCUK Research Fellowships

"Theory and Simulation of Materials"

Imperial College London

Department of Physics and Department of Materials

Salary range: £36,200 to £40,430 per annum

Three RCUK Research Fellowships are available at Imperial College London for suitably qualified candidates in the broad area of Theory and Simulation of Materials, including but not confined to electronic structure and transport, atomistic simulation, nanostructured materials, biomaterials, functional and structural metals, semiconductors, ceramics, polymers, metamaterials, and microstructural evolution. We expect the successful applicants to become key participants in the new Thomas Young Centre, the London Centre for Theory and Simulation of Materials, encouraging research links and joint activities between participating colleges within the University of London. There are already excellent links to experimental groups at Imperial and to the London Centre for Nanotechnology.

Information about the RCUK Fellowship scheme, including eligibility criteria, is available at

http://www.rcuk.ac.uk/acfellow/.

Candidates should note that this scheme is only open to researchers supported on any type of fixed term grant funding and to holders of current fellowship awards or other researchers without current research support. Candidates with appropriate experience and a recognised research track record are encouraged to apply.

Further enquiries can be directed to Professors Mike Finnis, m.finnis@imperial.ac.uk,
Peter Lee, p.d.lee@imperial.ac.uk or Adrian Sutton, a.sutton@imperial.ac.uk.

All three RCUK fellowships are for a period of five years and lead to open- ended academic posts. Two of the posts will be held jointly between the Departments of Materials and Physics and are available from 1st October 2007. The third post will be held wholly within the Department of Materials and will be centred on modelling materials processing, and is available from 1st October 2006.

Application forms can be downloaded from

http://www3.imperial.ac.uk/employment/applicationformacademic.

A job description and an application form can also be obtained from Darakshan Khan, e-mail
d.khan@imperial.ac.uk, tel. +44 (0) 20 7594 6775, Imperial College London, Human Resources, Faculty of Engineering, South Kensington campus, London SW7 2AZ, to whom two copies of the completed applications (with curriculum vitae and the names and contact details of two referees) should be sent. Please quote ref: RCUK/TYC on all correspondence.

Closing date: 30 September 2006

Valuing diversity and committed to equality of opportunity

Post-Doctoral Position

Catalysis on Complex Oxide Surface

Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a postdoctoral position in theoretical chemistry and computational materials science. The ideal candidate would have significant experience in plane-wave-based density functional calculations. A PhD in theoretical physics, chemistry, or related field is required. He or she will be involved in a number of challenging research projects in the realms of heterogeneous catalysis and nanostructured surfaces (see e.g. PRL 95, 266104 (2005); PRL 95, 136101 (2005); PRL 95, 096102 (2005); Angew. Chem. Int. Ed. 44, 2790 (2005); Angew. Chem. Int. Ed. 43, 6641 (2004) for recent work). The project will strongly benefit from collaborations with other theory groups as well as experimental groups within our Collaborative Research Center SFB 558 "Metal-substrate interactions in heterogeneous catalysis" (see: http://www.sfb558.de). Information on the techniques used and developed at the Center for Theoretical Chemistry are accessible via http://www.theochem.rub.de/go/cprev.html

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary research environment and excellent facilities including several high-performance parallel platforms in house, see

http://www.theochem.rub.de.

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references to

Dr. Bernd Meyer or Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de

The position is available immediatly. The appointment is initially for one year, with the possibility of renewal of at least two more years. Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Staff and Postdoctoral Positions

Center for Quantum Simulation Sciences (CQSS)

Institute of Physics, Chiense Academy of Sciences

Beijing 100080, China

Applications are invited for serveral staff and postdoctoral psitions at the Center for Quantum Simulation Sciences (CQSS), Institute of Physics, Chinese Academy of Science. The CQSS was newly founded in 2005 to promote the activities in the computational condensed matter physics. The center has presently 2 research groups and 6 staffs with strong on-going activities, especially for the surface sciences and the strongly correlated systems (see the homepage

http://cqss.iphy.ac.cn/

for details). The center is equipped with a powerful IBM SP690 supercomputer. Accompanying witht the 3-rd Innovation Program of the Chinese Academy of Sciences (2006-2010), the CQSS is expected to expand dynamically and will have a number of staff and postdoctoral positions open during the coming 5 years. We recruit young researchers with visible academic record and great potential in the computational condensed matter physics. Priorities will be given to candidates with background in (but not limited to):

(1) First-principles calculations based on density-functional theory (DFT).

(2) Molecular-dynamics simulations, large scale, multi-scale, etc.

(3) Beyond LDA: LDA+U, LDA+DMFT, GW, TDDFT, and etc.

(4) Quantum Monto Carlo Simulations.

The candidates will be offered with sizable starting grant depending on experience. While these positions are open essentially for Chinese researchers, people with other citizenship yet with strong background in the strategic areas of the center are also encouraged to apply. For further information and for applications, please send your CV, publication list, research plan, and arrange three letters of recommendations to the Director of the Center:

Prof. Zhong Fang
Director, Center for Quantum Simulation Sciences,
Insititute of Physics, Chinese Academy of Sciences,
Beijing 100080, China
Tel: +86-10-82648038
Fax: +86-10-62553698
Email: zfang@aphy.iphy.ac.cn.

Two Ph. D. Student Positions and Two Post-doctoral Positions
University of Nijmegen, The Netherlands

Two PhD student positions and two post-doctoral positions are available in the Electronic Structure of Materials (ESM) group at the University of Nijmegen, The Netherlands. The activities of the ESM group are in the area of computational materials science employing primarily first principles electronic structure calculations. Emphasis is on fundamental new materials aspects, while at the same time strong links with experimental groups are maintained.

One Ph. D. position is in the area of surface electronic structure and involves collaboration with the scanning probe microscopy and the solid state chemistry groups. Current activities in this project comprise the electronic structure of nanoscopic particles of magnetite from biological origin and organic molecules absorbed on metallic surfaces.

The second Ph. D. position is in the area of a new generation of solar cells and is in close collaboration with the Laboratory of Electronic Components and Materials (ECTM) of Delft University of Technology and Helianthos b.v. (Arnhem). It aims to demonstrate a new concept for solar cells, based on semiconductor superlattices with integrated spectrum-selective absorbers. The Ph. D. student will investigate energy band structures of superlattices without and with the absorbers using first principles molecular dynamics as well as the GW method. Involvement with the fabrication of the computer designed superlattices in order to verify the computational results in a later stage is expected.

Two post-doctoral positions are in the areas of nano-spintronics (involving finite temperature properties of half-metallic ferromagnets as well as amorphous transition-metal-boron compounds), hydrogen storage materials, organic conductors etc. etc.

The Ph. D. positions are for a period of 4 years. Both post-doctoral positions are initially for a one-year period.

Contact information:

Please contact for positions 1, 3 and 4 : Prof. Dr. R.A. de Groot (R.degroot@science.ru.nl, telephone +31(0)243652211) or Dr. G. A. de Wijs (G.dewijs@science.ru.nl, telephone +31(0)243652984), both at ESM, IMM, RU Nijmegen, Toernooiveld 1, 6525ED Nijmegen, The Netherlands.

For the second position: Dr. M. Zeman, ECTM , Mekelweg 4, TU Delft, 2628CD Delft, The Netherlands, (M.Zeman@tudelft.nl, telephone +31(0)152782409), or one of the persons mentioned above.

Ph. D. Positions

Graduate School on Nano- and Physical Sciences

University of Modena and Reggio Emilia

and the S3 National Research Center of INFM-CNR

Modena, Italy

Applications are invited for several 3-year PhD positions within the Graduate School on Nano- and Physical Sciences at the University of Modena and Reggio Emilia and the S3 National Research Center (http://www.s3.infm.it/) of INFM-CNR in Modena, Italy.

The deadline for applications is October 10, 2006.

The School is structured in two curricula:

(a) Physics;
(b) Nanosciences and nanotechnologies.

The latter is a multidisciplinary course open to students with background in different fields (physics, chemistry, biology, engineering, etc.).

The Program of the School includes a strong component in theoretical and computational research, with emphasis on fundamental phenomena as well as applications within information technologies (nano/opto-electronics, nanomagnetism, nanomechanics, nanotribology, etc) and life sciences (nanobiophysics etc). We also emphasize development of methods and codes. One of the fellowships will be specifically devoted to novel applications of high performance scientific computing to the physics of nanosystems, in collaboration with the CINECA (http://www.cineca.it/) supercomputing center.

The Faculty in these fields includes

Profs. C.M. Bertoni (`http://www.s3.infm.it/scheda_new.php?ID_PERS=8`),
V. Bortolani (`http://www.s3.infm.it/scheda_new.php?ID_PERS=13`),
M. Ferrario (`http://www.s3.infm.it/scheda_new.php?ID_PERS=33`),
G. Goldoni (`http://www.s3.infm.it/scheda_new.php?ID_PERS=41`),
C. Jacoboni (`http://www.s3.infm.it/scheda_new.php?ID_PERS=42`),
P. Lazzeretti (http://www.chimica.unimo.it/personale/lazzeretti.htm),
(`http://www.s3.infm.it/scheda_new.php?ID_PERS=48`),
R. Magri (`http://www.s3.infm.it/scheda_new.php?ID_PERS=47`),
F. Manghi (`http://www.s3.infm.it/scheda_new.php?ID_PERS=48`),
(`http://www.s3.infm.it/scheda_new.php?ID_PERS=59`),
E. Molinari (`http://www.s3.infm.it/scheda_new.php?ID_PERS=53`),

S. Ossicini (`http://www.s3.infm.it/scheda_new.php?ID_PERS=59`),
A. Ruini (`http://www.s3.infm.it/scheda_new.php?ID_PERS=72`).

For further information contact:

Prof. Stefano Ossicini (`http://www.s3.infm.it/scheda_new.php?ID_PERS=59`) (Director of the Ph. D. Course in Physics) or
Prof. Elisa Molinari (`http://www.s3.infm.it/scheda_new.php?ID_PERS=53`) (Director of the Ph. D. Course in Nanosciences and Nanotechnologies), or segreterias3@unimore.it.

Prof. Stefano Ossicini
Dipartimento di Scienze e Metodi dell'Ingegneria
Università di Modena e Reggio Emilia
Via G. Amendola 2
42100 Reggio Emilia-Italy

Postdoctoral Research Position in Computational Materials Physics, National Renewable Energy Laboratory, Golden, Colorado, USA

A postdoctoral position is available immediately to work with Drs. Yanfa Yan and Mowafak Al-Jassim at the National Renewable Energy Laboratory. The initial assignment is for one year, but renewable upon funding availability and performance. The research projects focus on the applications of ab initio calculations for the investigation of optical transport properties and impurity doping of wide-gap semiconductors. The candidates should have deep knowledge in ab initio calculations based on DFT, as well as a good experience with modeling codes such as WIEN2k and VASP. Accomplished research work in the field of impurity doping and optical transport is highly desirable. Interested candidates should send a full CV and arrange for three letters of references to

Dr. Yanfa Yan (`yanfa_yan@nrel.gov`)
or Dr. Mowafak Al-Jassim (`Mowafak_aljassim@nrel.gov`)
National Renewable Energy Laboratory
1617 Cole Blvd, Golden, Colorado, USA

Permanent Research Fellow Position

CEA-Saclay, France

A permanent Research Fellow position is available in the theoretical group of Modelisation of Surfaces, Interfaces and Nanostructures (MSIN) of the laboratory Service de Physique et Chimie des Surfaces et Interfaces (SPCSI), at CEA-Saclay (http://www-drecam.cea.fr/spcsi/), France.

Profile:

We are looking for an expert in ab-initio calculations (DFT-based methods), having a strong expertise in coding and development of codes and willing to apply such numerical techniques to the study of realistic systems in relation to electronic transport and/or excitations in nano-objects (atomic contacts, single molecules, clusters).

The successful candidate will join the MSIN group and will be expected to strongly interact with the members of the group, for example by

(i) implementing new theoretical approaches developed in our group,
(ii) using ab-initio calculations to extract relevant parameters for model Hamiltonians,
(iii) developing codes for nanoscale electronic transport.

The successful candidate will then strengthen the existing research activities of our group and will also be expected to develop collaborations with experimental groups of SPCSI on the following topics:

- quantum transport in nanostructures and molecular nanojunctions,
- electronic and optical excitation spectroscopies in nanoscale objects,
- interaction and organization at the molecule/surface interface.

Background:

The applicants should hold a Ph. D., have postdoctoral research experience and should have a proven track-record of cutting-edge research (in theoretical condensed-matter physics/chemistry, or a related field), including an ability to interact effectively within a research team involving experimentalists as well as other theoreticians.

Interested candidates are expected to send:

(1) Full CV
(2) List of publications.

To Dr C. Barreteau (cyrille.barreteau@cea.fr) and Dr H. Ness (herve.ness@cea.fr).

Informal enquiries are welcome and may be addressed to C. Barreteau and H. Ness.

Postdoctoral Position

Collaborative Research Centre 546 “Transition metal aggregates"

Humboldt University, Institute of Chemistry, Berlin, Germany

In the Collaborative Research Centre 546 “Transition metal aggregates" at Humboldt University, Institute of Chemistry,

(`www.chemie.hu-berlin.de/ag_sauer`)

a post-doctoral position (BAT-O IIa) is available for a computational physicist/chemist within Project C5 ‘Periodic DFT calculations of structure, dynamics and reactivity of vanadia aggregates". Funding is available till 30/06/2008, but an application will be made for another 3-years period.

The project includes DFT-calculations on models of supported transition metal oxide catalysts in close collaboration with experimental groups with the aims of identifying active surface species (V_2O_5, MoO_3, Nb_2O_5) and of clarifying the role of the oxide support (Al_2O_3, ZrO_2, CeO_2) in the catalytic activity of the catalysts. Excellent computer facilities are available.

The candidate is expected to have a PhD in Theoretical Physics/Chemistry/Materials Science and a strong background in ab-initio electronic structure methods for solids.

Applications with complete CV, list of publications and names with complete address of at least two references to Prof. Joachim Sauer (js@chemie.hu-berlin.de) or Dr. M. Veronica Ganduglia-Pirovano (vgp@chemie.hu-berlin.de) Humboldt-Universität zu Berlin, Institut für Chemie, Unter den Linden 6, 10099 Berlin

Postdoctoral Position

Humboldt University, Institute of Chemistry, Berlin, Germany

In the quantum chemistry group at Humboldt University, Institute of Chemistry, (`www.chemie.hu-berlin.de/ag_sauer`) a post-doctoral position (BAT-O IIa) is available for a computational chemist/physicist for 3 years from 1/10/2006.

The project includes modelling of adsorption and catalytic conversion of small molecules in known and new metal-organic framework structures. It is part of the EU MOFCAT project which provides opportunities for cooperation with experimental groups and other computational chemistry groups. Techniques that proved successful with zeolites, specifically QM/QM- and QM/MM-hybrid methods (PCCP 8, 2006, 3955-3965, see also `www.rsc.org/Publishing/ChemScience/Volume/2006/09/cracking_calculations.asp`) may be adapted. Participation in method developments is welcome, although not a condition.

We offer an excellent computing environment. The candidate is expected to have a PhD in Theoretical Chemistry/Physics and experience in (non-routine) applications of quantum chemical and simulation codes to complex systems.

Applications to: js@chemie.hu-berlin.de

Prof. Joachim Sauer, Humboldt-Universität zu Berlin, Institut für Chemie, Unter den Linden 6, 10099 Berlin.

Postdoctoral Associate Position in Computational and Experimental Materials Science

Department of Materials Science and Engineering

Massachusetts Institute of Technology, Cambridge MA, USA

The group of Professor Ceder, in the Department of Materials Science and Engineering, has several postdoctoral openings in the area of ab initio computations on materials. Research in the group spans a wide range of areas, from method development and fundamental materials science, to application of ab initio methods to the design materials in important areas of technology.

We are looking for people with background in first principles methodology. The candidates need to have either a strong background in the theory of modern ab initio methods (DFT, DFT+U and extensions), or an education in materials science with experience in the use of ab initio methods.

For an excellent candidate, a postdoc position may also be filled for experimental research in electrochemistry. In addition, for those that are interested, interaction with industry is also possible.

Starting dates are negotiable and can be anytime between Dec 1, 2006 and May 1, 2007.

Candidates should send a resume by email or postal mail with list of publications and names of references to:

Professor Gerbrand Ceder
Department of Materials Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Rm 13-5056
Cambridge MA -02139
USA
E-mail: gceder@mit.edu

EPSRC Ph. D. Studentship in Theoretical Nanoelectronics

Physics Department

Condensed Matter Theory Group at Lancaster University, UK

An EPSRC-funded three year PhD studentship is available from October 1st 2006 in Condensed Matter Theory Group at Lancaster University, under the supervision of Prof. Colin Lambert. The successful applicant will join a research team working on quantum electron transport through nanoscale systems, including single molecules, spintronic devices and carbon nanotubes. This project will interface with an EPSRC Basic Technology consortium "Controlled Electron Transport Through Single Molecules" and a 12-institution EC network, "Fundamental of Nanoelectronics."

Candidates should have, or be about to receive, an honours degree (at least 2.1 or equivalent) or higher in theoretical physics. The studentship offers full costs (fees plus stipend) for UK or EU citizens for 3 years.

Further details may be obtained by contacting Prof Colin Lambert (C.Lambert@Lancaster.ac.uk or tel. 01524 593059)

Details of the application procedure can be found on the Physics Department’s web site:

http://www.lancs.ac.uk/depts/physics/pgAdmissions/postgraduate.htm.

Closing Date: 1st October 2006

Postdoctoral Positions in LLNL’s Quantum Simulation Group

Lawrence Livermore National Laboratory’s (LLNL) Quantum Simulation Group is looking to fill one or more Postdoctoral Research Positions in the field of electronic structure simulations of materials. The positions are available immediately and renewable for up to 3 years.

We are seeking applicants with a strong background in solid-state physics or chemistry and experience with electronic structure simulation techniques such as Density Functional Theory and Quantum Monte Carlo. Candidates with experience studying nanostructured materials, electron transport in semiconductors, or radiation detector materials are particularly encouraged to apply.

The Quantum Simulation Group currently consists of ten Ph.D.’s in condensed matter physics and chemistry. It has extensive collaborations with a broad range of international theoretical and experimental groups. The group makes extensive use of the world leading high performance computational facilities at LLNL. More information on the QSG group, its research, publications, and personnel can be found on the group website, www.llnl.gov/qsg

Interested candidates should send their curriculum vitae and list of references to:

Dr. Eric Schwegler, schwegler1@llnl.gov

LLNL offers a challenging environment and a competitive salary/benefits package. When contacting us, please mention where you saw this ad. LLNL is operated by the University of California for the National Nuclear Security Administration/Department of Energy. We are proud to be an equal opportunity employer with a commitment to workforce diversity.

Postdoctoral and Research Associate Positions in NREL's Solid State Theory Group with Alex Zunger

Research Fields :
(1) Theory of Nanostructures
(2) Alloy Theory
(3) Magnetism and conductivity in Oxides

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

NREL's Solid State Theory Group is looking to fill Postdoctoral and Research Associate positions (depending on qualifications). The research area covers the theory of nanostructures, alloy theory, and magnetism and conductivity in oxides. The positions are available immediately and renewable upon mutual consent for up to 3 years. The salary range is $48,000 - $62,000 per year, depending on seniority, qualification and experience. Applicants are expected to have a strong background in solid-state theory and preferably in the area of nanostructures. For more details about ongoing work, see

http://www.sst.nrel.gov.

The Solid State Theory Group is headed by Alex Zunger and 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 now their curriculum vitae, list of publications (including preprints of unpublished papers, if possible), and arrange for two to three references addressed to:

Dr. 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`
(mailto: `gabriel_bester@nrel.gov`).

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

One Postdoctoral Position

"DFT rational exploration of hydride materials for on-vehicle hydrogen storage"

Applied Chemistry and Physical Chemistry R&D Division
Institut Françaís du Pétrole (IFP), France

One post-doctoral position is available in the Applied Chemistry and Physical Chemistry R&D Division at Institut Françaís du Pétrole (IFP) under the supervision of Dr. Pascal Raybaud. The position is opened from September 2006 and is initially funded for twelve months (eventually renewable for six months).

The candidate should be skilled in DFT based calculations applied to inorganic materials and/or organometallic compounds. The theoretical work is part of a new project led by IFP and funded by the French National Research Agency (ANR) within the framework of the Hydrogen program. The other partners are academic laboratories with expertise in the synthesis and characterization of hydride materials, and the Peugeot (PSA) motor company. The theoretical simulations of the thermodynamic and kinetic properties of light hydride materials are expected to furnish rational guides for experimentalists to synthesize new materials with high hydrogen weight capacities and reversible hydrogen absorption in ambient conditions. To meet these challenges, interactions with the experimental teams will be highly encouraged.

Motivated candidates are invited to send their CV including a list of publications and a brief description of research experience to:

Dr. Pascal Raybaud
Institut Françaís du Pétrole
Direction Chimie et Physico-Chimie Appliquées
Département Thermodynamique et Modélisation Moléculaire
1 & 4 Avenue de Bois Préau
92852 Rueil-Malmaison, FRANCE
Phone : +33 (0)1.47.52.71.84
Fax : +33 (0)1.47.52.70.58
Email: pascal.raybaud@ifp.fr
http://www.ifp.fr

Head of a Junior Research Group on "Ab initio Computation of Novel Materials"

Max-Planck-Institut für Festkörperforschung
Max Planck Institute for Solid State Research

The Max-Planck-Institute for Solid-State Research invites applications for the position as head of a Junior Research Group on "Ab initio Computation of Novel Materials".

The applicant is assumed to be a recognized researcher with excellent knowledge of condensed-matter theory and working experience with ab initio (e.g. density-functional-based) computation of the structure and dynamics of novel materials. Of particular interest are systems with reduced dimensionality and nanostructured materials.

The appointment will be for 5 years; an extension is possible. Remuneration will be paid at the associate professor level (W2) with all fringe benefits of the German public sector. The position includes an independent budget for personnel, running costs, and investment, office space for students and postdocs, and use of the research infrastructure of the institute.

The Max Planck Society seeks to increase the number of women in those areas where they are underrepresented and therefore explicitly encourages women to apply. The Max Planck Society is committed to employing more handicapped individuals and especially encourages them to apply.

Please send your application by October 31, 2006 to:

Max Planck Institute for Solid State Research
Managing Director
Heisenbergstr. 1
D-70569 Stuttgart, Germany

DIE ZEIT, 07.09.06

FACULTY POSITION IN SEMICONDUCTOR NANOSTRUCTURES

Institut National des Sciences Appliquées de Rennes (INSA), France

The Institut National des Sciences Appliquées de Rennes (INSA), a university centre with programs for all graduate levels (Bachelor, Master and Ph. D.), is inviting candidates to apply for a permanent Professor-researcher position.

The research area is on Semiconductor Nanostructures : III-V, germanium and silicon materials, Quantum dots (QD) and wells (QW).

The successful candidate will have demonstrated potential to develop strong programs of materials for photonics in applied and fundamental research. Individuals with expertise in materials processing and characterization in thin films, multilayers and nano-particles are encouraged to apply.

PLACE OF EMPLOYMENT: INSA, Rennes (Brittany) west of France.

WORKING LANGUAGE: French is the working language. English is essential.

SALARY : Salary is in accordance with the current collective agreement in France.

MODALITY :

All applications will be treated confidentially and a response will be given in May 2007.

Interested applicants should forward a complete curriculum vitae, a copy of their 3 most representative publications, a 1 to 2 page description of their research interests, as well as the names and addresses of 3 references before November, 2006 to :

INSA- Rennes, laboratoire LENS
20, Avenue des Buttes de Coesmes
35043 Rennes Cedex FRANCE
Or to:
slimane.loualiche@insa.rennes.fr

To be an eligible candidate, applicants must submit an initial declaration of interest with a national board (CNU : conseil national des Universités). To register, this candidate has to declare his interest via the government site (between September and October, 2006) and submit the required documents before December 15, 2005 with the CNU. The information in French detailing this procedure can be found at this address :

http://www.legifrance.gouv.fr/WAspad/UnTexteDeJorf?numjo=MENP0500924A

Postdoctoral Position at UC Santa Barbara

A postdoctoral position in Computational Materials Physics is available to work with Prof. Chris Van de Walle in the Solid State Lighting and Energy Center at the University of California, Santa Barbara (UCSB). Candidates should have experience with electronic structure and condensed matter theory. They should also have a keen interest in materials physics and a motivation to interact with experimentalists. Good communication skills (writing papers, making presentations) are required.

The project will encompass first-principles calculations (density-functional theory) for surfaces, interfaces, and point defects; development/application of techniques to overcome band-gap problems; and modeling of device structures, including Schroedinger-Poisson simulations and/or k.p calculations of band structure.

Applications should include: (1) Curriculum Vitae, (2) Publication List, (3) One-page summary of accomplishments to date, and their significance, (4) Names and contact information (including email) of three references.

Professor Van de Walle's group currently has five members and works on a variety of topics ranging from new materials for solid-state light emitters to hydrogen-storage materials. The Solid State Lighting and Energy Center, directed by Profs. S. Nakamura and S. DenBaars, comprises more than 50 researchers, including faculty, visitors, postdocs and graduate students, and is focused on developing novel technologies for solid-state light emitters and energy conversion. The UCSB campus offers a unique environment, both in terms of collaborative research and natural beauty. Competitive salaries are offered, based on qualifications and experience.

More information about UCSB, about the Solid State Lighting and Energy Center, and about the Materials Department can be found at www.ucsb.edu http://www.ucsb.edu/ , http://ssldc.ucsb.edu, and http://www.materials.ucsb.edu. Information about Prof. Van de Walle's research group can be found at

`http://www.mrl.ucsb.edu/~vandewalle`.

For more information or to apply, please contact Prof. Chris Van de Walle (vandewalle@mrl.ucsb.edu).

Chris G. Van de Walle
Professor
Materials Department
University of California
Santa Barbara, CA 93106-5050

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Fax: (805) 893-8983
E-mail: vandewalle@mrl.ucsb.edu
`http://www.mrl.ucsb.edu/~vandewalle`

POSTDOCTORAL POSITION IN COMPUTATIONAL MATERIALS SCIENCE

Department of Chemical Engineering and Materials Science

University of Minnesota, USA

A postdoctoral position is now open in Prof. M. Cococcioni's group in the department of Chemical Engineering and Materials Science of the University of Minnesota. The work will mostly consist in the development of computational approaches based on (but not restricted to) Density Functional Theory and its LDA+U extension to study strongly correlated systems. Possible applications range from metallo-organic complexes (for molecular catalysis) to bulk transition-metal compounds. To apply to this position candidates must have a PhD in Physics, Chemistry, Materials Science or closely related subjects and demonstrate strong interests and skills in computer simulations. Good knowledge and experience with DFT as well as in the development and implementation of numerical approaches are highly appreciated. Expertise in programming (fortran 90/95 in particular) and familiarity with Linux/Unix environments are also preferred. The appointment is initially for one year with the possibility of extension to one more year. The position is available immediately but some flexibility on the starting date is offered depending on when it is fulfilled.

Candidates should send their curriculum vitae (including list of publications), description of their research activity and interests, and 2 to 3 recommendation letters to:

Prof. Matteo Cococcioni
Department of Chemical Engineering and Materials Science
University of Minnesota,
151 Amundson Hall
421 Washington Av SE
Minneapolis, MN 55455, USA

bf A Tenure-track Position at the Assistant Professor level
Department of Chemistry of Queen's University, Kingston, Ontario, Canada

The Department of Chemistry of Queen's University invites applications for a tenure-track position at the Assistant Professor level in the area of computational/theoretical chemistry. Applications should include a curriculum vitae, a statement of teaching experience and philosophy, and a statement of research interests including research proposals. It is the responsibility of applicants to have letters from at least three referees sent directly to the address below. The deadline for completed applications, including letters of reference, is November 10, 2006.

Applications and letters of reference should be sent to: Dr. Robert P. Lemieux, Acting Head, Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6.

Further information about this opportunity can be obtained by contacting the Acting Head at 613-533-2649 or depthead@chem.queensu.ca.

Additional information on the Department of Chemistry can be found at

http://www.chem.queensu.ca .

Tucker Carrington Jr.
Departement de chimie
Universite de Montreal
Case postale 6128
succursale Centre-ville
Montreal (Quebec) H3C 3J7
Canada

tel: (514) 343-2123
fax: (514) 343-7586
e-mail: Tucker.Carrington@umontreal.ca
`http://www.centrcn.umontreal.ca/~tucker/`

Postdoctoral Position

Rutgers University, New Jersey, USA

A postdoctoral position is available to begin as early as January 2007 in the group of David Vanderbilt in the Department of Physics and Astronomy at Rutgers University. The research will be in the general area of DFT-based computational studies of ferroelectric and piezoelectric materials, and may cover the construction of DFT-based models for describing high-strain perovskite piezoelectrics, the piezoelectric properties of alloys and solid solutions, the nonlinear dielectric properties of bulk and superlattice perovskites in finite electric field, and the properties of novel ferroelectric and multiferroic materials. Experience with density-functional electronic-structure methods is essential.

Interested applicants should email to dhv@physics.rutgers.edu with CV attached (PDF preferred), and should supply names and contact information for two or three references. Consideration of candidates will begin immediately and will continue until the position is filled.

Postdoctoral Position
in Computational Chemistry
Department of Chemistry, University of Salerno, Italy

Applications are invited for a postdoctoral position in computational chemistry in the group of Luigi Cavallo in the Department of Chemistry at the University of Salerno, Italy. The initial appointment is for one year, with the possibility to renew for a second year on the condition that research funds are available.

Candidates should have a Ph. D. in Chemistry, Physics, or related fields. A strong background in computational chemistry and programming skills are essential. The main theme of our research is to develop and apply state-of-the-art computational tools (electronic structure calculations, mainly) to achieve an understanding of reaction mechanisms and of intermolecular interactions. The systems of primary interest are organometallic complexes for homogeneous catalysis. For more information see

http://www.chem.unisa.it/groups/molnac/.

Interested candidates should send a letter of intent and a C.V. (by e-mail to lcavallo-at-unisa.it), and arrange for two letters of recommendation.

Postdoctoral Research Fellow
Nanoquanta Network of Excellence

The perspective postdoctoral research fellow will develop theoretical and numerical tools for the calculation of excitation spectra in condensed matter. The main aim of the project is the inclusion of many-body effects beyond the single quasi-particle picture, based on the Bethe-Salpeter equation and time-dependent density-functional perturbation theory. Code developement, documentation, and mainteinance for the forthcoming European Theoretical Spectroscopy Facility (ETSF) facility will be also part of the work.

The 18 months appointment will start Dec. 1, 2006 and end May 31 2008.

The work will take place within the Nanoquanta Network of Excellence (http://www.nanoquanta.eu) and the ETSF (see http://www.etsf.eu).

The net (after taxes) salary can vary between 1500 and 2500 Euro/month, according to the experience and the type of contract chosen.

For information and applications please contact Prof. Giovanni Onida (giovanni.onida@mi.infm.it), indicating in the subject "Nanonquanta Postdoc 2006".

6 Abstracts

A study of the competition between delocalized and spin-orbit splitting in the actinides $5f$ states

J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz,
Lawrence Livermore National Laboratory, Livermore, California 94550, USA.
G. van der Laan
Synchrotron Radiation Source, Daresbury Laboratory, Warrington, WA4 4AD, UK
A.L. Kutepov
Russian Federation Nuclear Center, Institute of Technical Physics (VNIITF),
Snezhinsk, Chelabinsk Region, Russia

Abstract

Synchrotron-radiation-based X-ray absorption, electron energy-loss spectroscopy in a transmission electron microscope, multi-electronic atomic spectral simulations and first principles calculations (Generalized Gradient Approximation in the Local Density Approximation, GGA/LDA) have been used to investigate the electronic structure of the light actinides: α-Th, α-U and α-Pu. It will be shown that the spin-orbit interaction can be used as a measure of the degree of localization of valence electrons in a material. The spin-orbit interaction in the light actinide metals, α-Th, α-U and α-Pu, has been determined using the branching ratio of the white line peaks of the $N_{4,5}$ edges, which correspond to $4d \rightarrow 5f$ transitions. Examination of the branching ratios and spin-orbit interaction shows that the apparent spin-orbit splitting is partially quenched in α-U, but is strongly dominant α-Pu. These results are fully quantified using the sum rule. This picture of the actinide $5f$ electronic structure is confirmed by comparison with the results of electronic structure calculations forα-Th, α-U and α-Pu, which in turn are supported by a previous Bremstrahlung Isochromat Spectroscopy (BIS) experiment.

Published in *Recent Advances in Actinide Science,* Eds: R. Alvarez, N.D. Bryan and I. May, (RSC Publishing, ISBN 085404678X) pp. 719-721 (2006).
Copies available from g.vanderlaan@dl.ac.uk

Organometallic Benzene-Vanadium Wire:
A One-Dimensional Half-Metallic Ferromagnet

Volodymyr V. Maslyuk[1], Alexei Bagrets[2,1], Velimir Meded[2,3],
Andreas Arnold[2], Ferdinand Evers[2,4], Mads Brandbyge[5],
Thomas Bredow[6], and Ingrid Mertig[1]
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D-76128 Karlsruhe, Germany
[5]*NanoDTU, MIC – Department of Micro and Nanotechnology,*
Technical University of Denmark, DK-2800 Lyngby, Denmark
[6]*Institut für Theoretische Chemie, Universität Hannover,*
D-30167 Hannover, Germany

Abstract

Using density functional theory we perform theoretical investigations of the electronic properties of a freestanding one-dimensional organometallic vanadium-benzene wire. This system represents the limiting case of multidecker $\mathrm{V}_n(\mathrm{C}_6\mathrm{H}_6)_{n+1}$ clusters which can be synthesized with established methods. We predict that the ground state of the wire is a 100% spin-polarized ferromagnet (half-metal). Its density of states is metallic at the Fermi energy for the minority electrons and shows a semiconductor gap for the majority electrons. We find that the half-metallic behavior is conserved up to 12% longitudinal elongation of the wire. Ab initio electron transport calculations reveal that finite size vanadium-benzene clusters coupled to ferromagnetic Ni or Co electrodes will work as nearly perfect spin filters.

[Physical Review Letters **97**, 097201 (2006)]

Contact person: Alexei Bagrets (alexej.bagrets@int.fzk.de)

Structural and chemical embrittlement of grain boundaries by impurities: a general theory and first principles calculations for copper

A. Y. Lozovoi(1), A. T. Paxton(1), and M. W. Finnis(2)
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Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, U.K.
(2) *Department of Materials, Imperial College of Science,*
Technology and Medicine, Exhibition Road, London SW7 2AZ, U.K.

Abstract

First principles calculations of the $\Sigma5(310)[001]$ symmetric tilt grain boundary in Cu with Bi, Na, and Ag substitutional impurities provide evidence that in the phenomenon of Bi embrittlement of Cu grain boundaries electronic effects do not play a major role; on the contrary, the embrittlement is mostly a structural or "size" effect. Na is predicted to be nearly as good an embrittler as Bi, whereas Ag does not embrittle the boundary in agreement with experiment. While we reject the prevailing view that "electronic" effects (*i.e.*, charge transfer) are responsible for embrittlement, we do not exclude the rôle of chemistry. However numerical results show a striking equivalence between the alkali metal Na and the semi metal Bi, small differences being accounted for by their contrasting "size" and "softness" (defined here). In order to separate structural and chemical effects unambiguously if not uniquely, we model the embrittlement process by taking the system of grain boundary and free surfaces through a sequence of precisely defined *gedanken* processes; each of these representing a putative mechanism. We thereby identify *three* mechanisms of embrittlement by substitutional impurities, two of which survive in the case of embrittlement or cohesion enhancement by interstitials. Two of the three are purely structural and the third contains both structural and chemical elements that by their very nature cannot be further unravelled. We are able to take the systems we study through each of these stages by explicit computer simulations and assess the contribution of each to the nett reduction in intergranular cohesion. The conclusion we reach is that embrittlement by both Bi and Na is almost exclusively structural in origin; that is, the embrittlement is a size effect.

(Accepted for Phys. Rev. B; see also preprint cond-mat/0608508)
Contact person: A. Y. Lozovoi (s.lozovoi@qub.ac.uk)

Anisotropic x-ray magnetic linear dichroism at the Fe $L_{2,3}$ edges in Fe_3O_4

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Advanced Light Source, Lawrence Berkeley National Laboratory,
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Gerrit van der Laan
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Warrington WA4 4AD, United Kingdom
Rajesh V. Chopdekar and Yuri Suzuki
Department of Materials Science and Engineering, UC Berkeley,
Berkeley, CA 94720

Abstract

X-ray magnetic linear dichroism at the Fe $L_{2,3}$ edges of the ferrimagnet Fe_3O_4 was found to exhibit a strong dependence on the relative orientation of external magnetic field, x-ray polarization, and crystalline axes. Spectral shape and magnitude of the effect were determined for Fe_3O_4(011) and Fe_3O_4(001) thin films varying the in-plane orientation of field and polarization. All dichroism spectra can be described as a linear combination of two fundamental spectra which in turn give a good agreement with calculated spectra using atomic multiplet theory. The angular dependence of the magnetic dichroism reflects the crystal field symmetry. It can be used to estimate the crystal field splitting and allows determining the spin quantization axis.

Published in Physical Review B **74**, 094407 (2006).
Reprints available from g.vanderlaan@dl.ac.uk

Relativistic treatment of spin-currents and spin-transfer torque

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Technical University Vienna, Gumpendorferstr. 1a, A-1060 Vienna, Austria
[2] *H. H. Wills Physics Laboratory, University of Bristol,*
Tyndall Avenue, Bristol BS8 1TL, United Kingdom

Abstract

It is shown that a useful relativistic generalization of the conventional spin density $\vec{s}(\vec{r},t)$ for the case of moving electrons is the expectation value $(\vec{\mathcal{T}}(\vec{r},t),\,\mathcal{T}_4(\vec{r},t))$ of the four-component Bargmann-Wigner polarization operator $T_\mu = (\vec{T}, T_4)$ with respect to the four components of the wave function. An exact equation of motion for this quantity is derived, using the one-particle Dirac equation, and the relativistic analogues of the non-relativistic concepts of spin-currents and spin-transfer torques are identified. In the classical limit the time evolution of $(\vec{\tau}, \tau_4)$, the integral of $(\vec{\mathcal{T}}(\vec{r},t),\,\mathcal{T}_4(\vec{r},t))$ over the volume of a wave packet, is governed by the equation of motion first proposed by Bargmann, Michel and Telegdi generalized to the case of inhomogeneous systems. In the non-relativistic limit it is found that the spin-current has an intrinsic Hall contribution and to order $1/c^2$ a spin-orbit coupling related torque appears in the equation of motion for $\vec{s}(\vec{r},t)$. The relevance of these results to the theory of the intrinsic spin Hall effect and current-induced switching are briefly discussed.

(Submitted to PRL)
Contact person: av@cms.tuwien.ac.at

Copper oxidation state in chalcopyrite: Mixed Cu d^9 and d^{10} characteristics

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School of Earth, Atmospheric and Environmental Sciences
and Williamson Research Centre for Molecular Environmental Science,
University of Manchester, Manchester M13 9PL, UK
G. van der Laan
CCLRC Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

The determination of the oxidation states of copper and iron in sulfides, and chalcopyrite ($CuFeS_2$) in particular, using $2p$ X-ray photoemission spectroscopy (XPS) and $L_{2,3}$ edge X-ray absorption spectroscopy (XAS) is revisited. Reassessment of the published spectra derived by these methods produces consistent results and reveals the d count in the copper compounds to be intermediate between d^9 and d^{10}. Nevertheless, these covalent copper compounds can be divided into those nominally monovalent and those nominally divalent. The Fe $L_{2,3}$ edge XAS of chalcopyrite, along with Mössbauer data, confirm the presence of high-spin Fe^{3+}. Chalcopyrite, despite recent published reports to the contrary, clearly belongs to the monovalent copper class.

Published in Geochimica et Cosmochimica Acta **70**, 4635–4642 (2006)
Reprints available from g.vanderlaan@dl.ac.uk

An Ab-initio theory for the temperature dependence of magnetic anisotropy

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Abstract

We present a first-principles theory of the variation of magnetic anisotropy, K, with temperature, T, in metallic ferromagnets. It is based on relativistic electronic structure theory and calculation of magnetic torque. Thermally induced 'local moment' magnetic fluctuations are described within the relativistic generalisation of the 'disordered local moment' (R-DLM) theory from which the T dependence of the magnetisation, m, is found. We apply the theory to a uniaxial magnetic material with *tetragonal* crystal symmetry,$L1_0$-ordered FePd, and find its uniaxial K consistent with a magnetic easy axis perpendicular to the Fe/Pd layers for all m and proportional to m^2 for a broad range of values of m. This is the same trend that we have previously found in $L1_0$-ordered FePt and which agrees with experiment. We also study a magnetically soft *cubic* magnet, the $Fe_{50}Pt_{50}$ solid solution, and find that its small magnetic anisotropy constant K_1 rapidly diminishes from 8 μeV to zero. K evolves from being proportional to m^7 at low T to m^4 near the Curie temperature. The accounts of both the tetragonal and cubic itinerant electron magnets differ from those extracted from single ion anisotropy models and instead receive clear interpretations in terms of two ion anisotropic exchange.

(The manuscript is to appear in Phys.Rev.B)
A preprint is available on cond-mat/0606219
Further information about the work can be obtained via email to **j.b.staunton@warwick.ac.uk**.

Construction of Wannier functions from localized atomic-like orbitals

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Abstract

The problem of construction of the Wannier functions (WFs) in a restricted Hilbert space of eigenstates of the one-electron Hamiltonian $\hat{H}$ (forming the so-called low-energy part of the spectrum) can be formulated in several different ways. One possibility is to use the projector-operator techniques, which pick up a set of trial atomic orbitals and project them onto the given Hilbert space. Another possibility is to employ the downfolding method, which eliminates the high-energy part of the spectrum and incorporates all related to it properties into the energy-dependence of an effective Hamiltonian. We show that by modifying the high-energy part of the spectrum of the original Hamiltonian $\hat{H}$, which is rather irrelevant to the construction of WFs in the low-energy part of the spectrum, these two methods can be formulated in an absolutely exact and identical form, so that the main difference between them is reduced to the choice of the trial orbitals. Concerning the latter part of the problem, we argue that an optimal choice for trial orbitals can be based on the maximization of the site-diagonal part of the density matrix. This idea is illustrated for a simple toy model, consisting of only two bands, as well as for a more realistic example of t_{2g} bands in V_2O_3. Using the model analysis, we explicitly show that a bad choice of trial orbitals can be linked to the *discontinuity* of phase of the Bloch waves in the reciprocal space, which leads to the delocalization of WFs in the real space. Nevertheless, such a discontinuity does not necessary contribute to the matrix elements of $\hat{H}$ in the Wannier basis. Similar tendencies are seen in realistic calculations for V_2O_3, though with some variations caused by the multi-orbital effects. An analogy with the search of the ground state of a many-electron system is also discussed.

(Submitted to Phys. Rev. B)
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The manuscript is also available as cond-mat/0608528

Correlation Energies in Distorted $3d$-t_{2g} Perovskite Oxides

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Abstract

Using an effective low-energy Hamiltonian derived from the first-principles electronic structure calculations for the narrow t_{2g} bands of YTiO$_3$, LaTiO$_3$, YVO$_3$, and LaVO$_3$, we evaluate the contributions of the correlation energy (E_C) to the stability of different magnetic structures, which can be realized in these distorted perovskite oxides. We consider two approximations for E_C, which are based on the regular perturbation theory expansion around a nondegenerate Hartree-Fock ground state. One is the second order of perturbation theory, which allows us to compare the effects of local and nonlocal correlations. Another one is the local t-matrix approach, which allows us to treat some higher-order contributions to E_C. The correlation effects systematically improve the agreement with the experimental data and additionally stabilize the experimentally observed G- and C-type antiferromagnetic (AFM) structures in YVO$_3$ and LaVO$_3$, though the absolute magnitude of the stabilization energy is sensitive to the level of approximations and somewhat smaller in the t-matrix method. The nonlocal correlations additionally stabilize the ferromagnetic ground state in YTiO$_3$ and the C-type AFM ground state in LaVO$_3$. Amongst two inequivalent transition-metal sites in the monoclinic structure, the local correlations are stronger at the sites with the least distorted environment. Limitations of the regular perturbation-theory expansion for LaTiO$_3$ are also discussed.

(Submitted to Phys. Rev. B)
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The manuscript is also available as cond-mat/0608625

Transport Properties of (Ga,Mn)As Diluted Magnetic Semiconductors in the Bulk and in Layered Systems

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Abstract

Transport properties of systems based on diluted magnetic semiconductors (Ga,Mn)As are investigated theoretically by means of the Kubo linear response theory. The underlying electronic structure is obtained within the local spin-density approximation using the scalar-relativistic tight-binding linear muffin-tin orbital (TB-LMTO) method. The effect of substitutional randomness on the electronic structure and on the transport properties is systematically described in the coherent potential approximation (CPA). The quantities studied include the residual resistivities of the bulk alloys as well as conductances of epitaxial trilayers Cr/(Ga,Mn)As/Cr (001) in the current-perpendicular-to-plane (CPP) orientation. The results witness that various compensating defects such as As antisite atoms and Mn interstitials have much stronger detrimental effect on the spin polarization of the CPP conductances as compared to their influence on the spin polarization of the bulk conductivities.

(To be published in Materials Science Forum)

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Local moments, exchange interactions, and magnetic order in Mn-doped $LaFe_2Si_2$ alloys

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Abstract

Formation of local magnetic moments in the intermetallic compound $LaFe_2Si_2$ due to doping by a few at. % of Mn has been investigated by theoretical and experimental tools. While a number of low-temperature experiments proves appearance of non-zero magnetic moments due to the Mn doping, the measured ^{57}Fe Mössbauer spectra rule out sizable local moments of Fe atoms. This conclusion is in agreement with results of first-principles electronic structure calculations that yield non-vanishing moments only on Mn atoms. The calculated Mn-Mn exchange interactions are of both signs which indicates a magnetically frustrated ground state, probably with a spin glass-like arrangement of the Mn moments.

To be published in: J. Magn. Magn. Mater.
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Development of high-temperature thermoelectric materials based on $SrTiO_3$-layered perovskites

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Abstract

For improving the performance of ceramic thermoelectric materials the increase of the effective mass is required, because it is the main factor determining the Seebeck coefficient, in the case of a semiconductor with sufficiently high carrier concentration. The Ruddlesden-Popper phase $Sr_3Ti_2O_7$, with its conducting perovskites layer in between the phonon absorbing SrO layers, is an example for advanced material design by nano-block integration. Using ab-initio simulations, the electronic bandstructure was calculated, and from the curvature of the bands the effective mass was deduced. While Sr3Ti2O7 has a smaller effective mass than the Nb-doped $SrTiO_3$, the layered perovskites with substitution of Ta instead of Ti possess very large effective masses (m^*/m_0 = 9 in average) and a large thermopower is expected.

Published in: International Journal of Materials Research (former Zeitschrift für Metallkunde) **97** (2006) 5 657-662. Contact person: wi-wunder@rocketmail.com

First-principles statistical mechanics study of the stability of a sub-nanometer thin surface oxide in reactive environments: CO oxidation at Pd(100)

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Abstract

We employ a multiscale modeling approach to study the surface structure and composition of a Pd(100) model catalyst in reactive environments. Under gas phase conditions representative of technological CO oxidation ($\sim$ 1 atm, 300-600 K) we find the system on the verge of either stabilizing sub-nanometer thin oxide structures or CO adlayers at the surface. Under steady-state operation this suggests the presence or continuous formation and reduction of oxidic patches at the surface, which could be key to understand the observable catalytic function.

(submitted to: Phys. Rev. Lett.)
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Epitaxy of Mn on Si(001): Adsorption, surface diffusion, and magnetic properties studied by density-functional theory

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Abstract

Ultrathin films of manganese-silicides on silicon are of relevance as a possible material system for building spintronics devices with silicon technology. For the initial growth of such films on Si(001), total-energy calculations are presented using density-functional theory and the *full-potential augmented plane wave plus local orbital* method. For adsorption of a single Mn atom we find that binding at the subsurface site below the Si surface dimers is about 0.9 eV stronger than on-surface adsorption. There is an energy barrier of only 0.3 eV for adsorbed Mn to go sub-surface, and an energy barrier of 1.2 eV for the reverse process. From the calculated potential-energy surface for the Mn adatom we conclude that the most stable site *on* the surface corresponds to the hollow site where Mn is placed between two Si surface dimers. For on-surface diffusion both along and perpendicular to the Si dimer rows, the Mn atoms have to overcome energy barriers of 0.65 eV. For coverages of 0.5 monolayers (ML) or higher, we find that the Si dimers of the Si(001) surface are broken up, and a mixed MnSi layer becomes energetically the most favorable structure. For coverages above 1 ML, the lowest-energy structure changes to a pure Mn subsurface layer, capped by a layer of Si adatoms. We identify this transition with the onset of Mn-silicide formation in an epitaxially stabilized CsCl-like crystal structure. Such MnSi films are found to have sizable magnetic moments at the Mn atoms near the surface and interface, and ferromagnetic coupling of the Mn magnetic moments within the layers. Layer-resolved electronic densities-of-states are presented that show a high degree of spin polarization at the Fermi level, up to 45% and 27% for films with two or three Si–Mn layers, respectively.

(submitted to: Phys. Rev. B)

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Transition-metal silicides as novel materials for magnet-semiconductor heterostructures

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Abstract

The injection of a spin-polarized current into a semiconductor, one of the key requirements for spintronics, poses the challenge for computational materials science to screen possibly suitable materials. In a number of theoretical investigations, we have put forward magnetic intermetallic compounds grown epitaxially on Si as promising candidates. We employed density functional theory calculations with the GGA-PBE exchange-correlation functional and the full-potential augmented wave plus local orbital (FP-APW+lo) method, as implemented in the WIEN2k package. In the spirit of computational materials science, we investigated the stability and magnetic properties of thin films of the Heusler alloy Co_2MnSi, as well as of binary late transition metal monosilicides, in contact with the Si surface. For the Heusler alloy Co_2MnSi, we could show that the (001) surface retains the half-metallic character of the bulk if a fully Mn-terminated surface is prepared. At interfaces with Si, a finite density of states at the Fermi energy was found for both spin channels, but the half-metallic behavior recovers only a few layers away from the interface. For the monosilicides of the late $3d$-transition metals (Mn, Fe, Co, Ni), we predict a novel CsCl-like structure that may be stabilized epitaxially on Si(001). For very thin films of CoSi and MnSi grown in this structure, our calculations find a ferromagnetic ground state. Recently, we identified the atomic structure of MnSi films on Si(111) which is close to the natural crystal structure of bulk MnSi (B20), and also shows large magnetic moments of the Mn atoms at the surface and interface. All MnSi films have a high degree of spin polarization (between 30% and 50%, depending on film thickness) at the Fermi level, and are thus promising materials for fabricating electrical contacts for spin injection into Si.

(submitted to: J. Appl. Phys.)

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X–ray Spectroscopic Fingerprints of Reactive Oxygen Sites at the $MoO_3(010)$ Surface

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Abstract

The identification of oxygen sites at metal oxide surfaces and the characterization of their properties is of great importance for an understanding of the catalytic activity of such materials and, thus, for a rational design of efficient and selective catalysts. In the case of the clean $MoO_3(010)$ surface we show that an unambiguous discrimination of the different reactive oxygen sites can be obtained by angle–resolved Near–Edge X–Ray Absorption Fine Structure (NEXAFS) combined with Density–Functional–Theory (DFT) based spectrum analyses for different photon polarization directions. In particular, we are able to unequivocally discriminate the characteristic spectral signatures of singly coordinated molybdenyl oxygen covering the topmost molybdenum layers from those of other oxygen centers that have very similar local environment and only differ by their spacial orientation in the crystal. Theoretical predictions are also successfully used to identify and interpret characteristic features in the NEXAFS spectra that arise from specific vacancy sites present at oxygen deficient surfaces.

(to appear in J. Catal.)
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Exact-exchange based quasiparticle energy calculations for the band gap, effective masses and deformation potentials of ScN

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Abstract

The band gaps, longitudinal and transverse effective masses, and deformation potentials of ScN in the rock-salt structure have been calculated employing G_0W_0-quasiparticle calculations using exact-exchange Kohn-Sham density functional theory one-particle wavefunctions and energies as input. Our quasiparticle gaps support recent experimental observations that ScN has a much lower indirect band gap than previously thought. The results are analyzed in terms of the influence of different approximations for exchange and correlation taken in the computational approach on the electronic structure of ScN.

(submitted to: Phys. Rev. B)

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Strain field calculations of quantum dots — a comparison study of two methods

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Abstract

The elastic strain field plays a crucial role during the self-organized growth of semiconductor quantum dot structures in the Stranski-Krastanov growth mode. Several theoretical methods have been developed for calculating the strain field of these lattice-mismatched systems. In this report we present a study exemplarily comparing an atomistic approach and calculations using elasticity theory. Features, limitations and selected possible applications of both approaches are discussed.

(To appear in: Proc. 28th Int. Conf. on the Physics of Semiconductors (ICPS 28), July 24-28, 2006, Vienna, Austria (2006).

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Theory of optical excitation and relaxation phenomena at semiconductor surfaces: linking Density Functional and Density Matrix Theory

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Abstract

A theory for the description of optical excitation and the subsequent phonon-induced relaxation dynamics of nonequilibrium electrons at semiconductor surfaces is presented. In the first part, the fundamental dynamical equations for electronic occupations and polarisations are derived using density matrix formalism for a surface-bulk system including the interaction of electrons with the optical field and electron-phonon interactions. The matrix elements entering these equations are either determined empirically or by Density Functional Theory (DFT) calculations. In the subsequent parts of the paper, the dynamics at two specific semiconductor surfaces is discussed in detail. The electron relaxation dynamics underlying a time-resolved two photon photoemission experiment at an InP surface is investigated in the limit of a parabolic four band model. Moreover, the electron relaxation dynamics at a Si(100) surface is analysed. Here, the coupling parameters and the band structure are obtained from DFT calculations.

(submitted to: Appl. Phys. A (in press))
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Improved hybrid algorithm with Gaussian basis sets and plane waves: First-principles calculations of ethylene adsorption on β-SiC(001)-(3$\times$2)

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Abstract

We present an algorithm for DFT calculations employing Gaussian basis sets for the wave function and a Fourier basis for the potential representation. In particular, a numerically very efficient calculation of the local potential matrix elements and the charge density is described. Special emphasis is placed on the consequences of periodicity and explicit **k**-vector dependence. The new algorithm is tested by comparison with more straightforward ones for the case of adsorption of ethylene on the silicon-rich SiC(001)-(3$\times$2) surface clearly revealing its substantial advantages. A complete self-consistency cyle is speeded up by roughly one order of magnitude since the calculation of matrix elements and of the charge density are accelerated by factors of ten and eighty, respectively, as compared to their straightforward calculation. Our results for C_2H_4:SiC(001)-(3$\times$2) show that ethylene molecules preferentially adsorb in *on-top* positions above Si dimers on the substrate surface saturating both dimer dangling bonds per unit cell. In addition, a twist of the molecules around a surface-perpendicular axis is slightly favored energetically similar to the case of a complete monolayer of ethylene adsorbed on the Si(001)-(2$\times$1) surface.

(submitted to Physical Review B)
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Adsorption of NO in Fe^{2+}-exchanged ferrierite. A Density Functional Theory Study.

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Abstract

The properties of the Fe-exchanged ferrierite are investigated by ab initio periodic DFT calculations. Stabilities of Al/Si substitutions are compared for all four irreducible tetrahedral (T-) sites of the framework. For each T-site the most stable position of the extra-framework Fe^{2+} cation is located in the six-membered ring in agreement with experimental data. Depending on the location of the framework Al/Si substitutions differences in total energies of Fe-exchanged configurations can be as high as 200 kJ/mol. Simulated adsorption of NO shows that both ON- and NO- interactions with Fe^{2+} are at least metastable. Adsorption through the N-atom, however, is 2.5-times stronger. Two types of Fe-exchanged configurations are observed. Stable configurations with the cation located in a β-site and exhibiting low adsorption energies of 180 kJ/mol, are destabilized upon adsorption of NO. Less stable configurations, with the cation located in an α-site, and exhibiting higher adsorption energies of 240 kJ/mol, are stabilized upon adsorption. A strong interaction of NO with Fe^{2+} can cause a migration of the extra-framework cation to a new position in the zeolite framework. The interaction of NO with the Fe^{2+} cation combines both σ- and the π-bonding. σ-bonding depletes the electron density in Fe-d_σ orbitals and leads to the accumulation in the N p_σ orbital. The π-bonding causes the increase of the π-electron density on both the N- and the Fe-atom. Adsorption induces extensive changes of the electron density distribution within the NO molecule. An expansion of the N p_σ density is accompanied with a depletion of the N p_π density oriented towards the O-atom. On the contrary, the O-atom exhibits a depletion of the σ-density and an increase of the π-density. The complex polarization of the N-O bond leads to only slight shortening of the bond length. Stretching frequencies calculated for configurations with different stability vary from 1866 cm^{-1} to 1909 cm^{-1}. For several stable configurations the calculated stretching frequency of 1876 cm^{-1} is in good agreement with the maximum of the IR band and for most configurations the frequency is within the width of the experimental band. Too high frequencies calculated for two Al atoms in small rigid ring indicate that no such configurations exist in ferrierite structures. The bonding of NO on the Fe^{2+} cation is qualitatively different from bonding on the surface of a transition metal characterized by the Blyholder scheme. The ïĄř-back donation on the surface leads to a weakening of the N-O bond and to a downshift of the stretching frequency. On the contrary, in the bonding of NO to a transition metal cation the electron density accumulates within the newly formed N-Fe bond depleting proportionally both the molecule and the cation. The withdrawing of antibonding electron density leads to a strengthening of the intramolecular bond and to higher N-O stretching frequencies.

(submitted to: J. Phys. Chem. B)
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First-principles study of elastic properties of CeO_2, ThO_2 and PoO_2

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Abstract

Using first-principles density functional calculations the structural and elastic properties of fluorite type oxides CeO_2, ThO_2 and PoO_2 were studied by means of the full-potential linear muffin-tin orbital method. Calculations were performed within the local density approximation (LDA) as well as generalised gradient approximation (GGA) to the exchange correlation potential. The calculated equlibrium lattice constants and bulk modulii are in good agreement with the experimental results, as are the computed elastic constants for CeO_2 and ThO_2. For PoO_2 this is the first quantitative theoretical prediction of the ground state properties, which still awaits experimental confirmation. The calculations find PoO2 to be a semiconductor with an indirect band gap and elastic constants similar in magnitude to those of CeO_2 and ThO_2.

(Accepted in J. Phys.: Condens. Matter)
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Calculated structural, elastic and electronic properties of $SrCl_2$

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Abstract

Density functional calculations have been performed to obtain the structural and electronic properties as well as elastic constants of cubic $SrCl_2$. The compound is found to be an insulator with an indirect band gap of 5.18 eV. The band gap initially increases and then decreases as a function of pressure. Calculated equilibrium properties such as lattice constant, bulk modulus and elastic constants are in good agreement with experimental studies. The calculated C_{44} value agrees well with experiment only when the chlorine atoms are allowed to displace under strain, indicating the importance of inner strain relaxation. From the elastic constants theoretical values of the Young's modulus, shear modulus, Poisson's ratio, sound velocities and Debye temperature of $SrCl_2$ are obtained.

(Submitted to Solid State Commun.)
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7 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Short-range correlations in disordered systems: the Non-local Coherent-Potential Approximation"

Short-range correlations in disordered systems: the nonlocal coherent-potential aproximation

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Abstract

A review of the nonlocal coherent-potential approximation (NLCPA) is presented for describing short-range correlations in substitutionally-disordered systems. Originally introduced by Jarrell and Krishnamurthy to generalise the widely used coherent-potential approximation (CPA) approach in the context of a tight-binding model, the NLCPA has since been implemented within KKR multiple scattering theory (KKR-NLCPA) and combined with density functional theory for *ab-initio* calculations (self-consistent-field (SCF)-KKR-NLCPA). Here an application to the $Cu_{50}Zn_{50}$ disordered alloy is described, demonstrating the role of charge transfer and the variation of the total energy as a function of chemical short-range order. Significantly, the method will enable important problems involving systems with spin, strain, or valency fluctuations to be tackled in a parameter-independent and material-specific way.

1 Introduction

In substitutionally-disordered systems such as the solid solution phase of an alloy, we are interested in configurationally-averaged properties. For example, for a binary solid solution we should in principle calculate properties for each of the 2^N possible configuations (where N is the number of sites in the lattice) and then take a statistical average according to the probability of each configuration occuring. Clearly this is a computationally impossible task and so some approximation scheme is needed. For many years the coherent-potential approximation (CPA) [1], a mean-field approach, has been widely used to deal with such an ensemble of disorder configurations. Its application within the multiple-scattering Korringa-Kohn-Rostoker [2, 3] (KKR) electronic structure method has been particularly successful. Indeed, the KKR-CPA [4, 5] and its LMTO derivatives are the only electronic structure methods which can deal with disordered systems and be combined with density functional theory (DFT) [6, 7] for *ab-initio* calculations. Such self-consistent-field (SCF)-KKR-CPA [8–11] calculations require, say for a binary solid solution, the self-consistent determination of two ‘partially-averaged’ single-site charge densities

$\overline{\rho}_A$ and $\overline{\rho}_B$ only, where the CPA treats the configurational averages over all possible chemical environments as a mean field. As well as application to a wide range of disordered alloys, the SCF-KKR-CPA has also been adapted to deal with the 'disordered local moment' spin fluctuations in itinerant magnets at finite temperature [12, 13]. However, despite numerous successes, the SCF-KKR-CPA has a serious limitation due to the single-site mean-field nature of the CPA itself, specifically it neglects correlations in the occupation of the lattice sites. It is therefore unable to include important short-range environmental effects present in the individual configurations into its configurationally-averaged description of the system. These include 1. chemical short-range order (SRO) i.e. the tendency for sites to either be surrounded by like sites (clustering) or by unlike sites (ordering) on short length scales, 2. charge correlations in alloys i.e. the Madelung contribution to the total energy, 3. lattice displacements in alloys i.e. deviations from the average rigid lattice due to size mis-match between the constituent atoms, and 4. correlations in the orientations of the local moments in metallic magnets at finite temperature.

The development of a satisfactory multi-site or cluster generalisation of the CPA in order to address this missing physics has remained a long-standing problem [14]. However, a recent theory, the nonlocal coherent potential approximation (NLCPA) [15], appears to possess all the attributes required for a satisfactory generalisation of the CPA. It was originally introduced by Jarrell and Krishnamurthy [15] in the context of a tight-binding model Hamiltonian as the static version of the dynamical cluster approximation (DCA) [16, 17] used for describing short-range dynamical correlations in the Hubbard model. The NLCPA was subsequently derived within the KKR framework [18], and the first KKR-NLCPA [18, 19] implementation for a realistic system was given in [20]. Moreover, the KKR-NLCPA has recently been combined with DFT and, significantly, the resulting SCF-KKR-NLCPA [21] method enables the total energy to be investigated as a function of chemical SRO. As a generalisation of the conventional SCF-KKR-CPA, it requires the self-consistent determination of a set of 'partially-averaged' cluster charge densities $\{\underline{\overline{\rho}}_\gamma\}$ where the NLCPA treats the configurational averages over all possible chemical environments as a mean field. Since possible charge transfer between the cluster sites can now be explicitly accounted for, the missing charge-correlation (Madelung) [22–25] electrostatic contribution to the total energy can be systematically taken into account as the cluster size increases. In addition to alloys, further important future developments include application to systems with spin fluctuations as mentioned above, and pseudo-alloy problems such as valency fluctuations [26].

Before summarising the contents of this highlight, it is worth mentioning some of the advantageous properties of the NLCPA which facilitates its application to the above problems. A key advantage of the NLCPA is that, like the conventional CPA, it preserves the full translational and point-group symmetry of the underlying lattice. This means the NLCPA is computationally feasible for realistic systems since the reciprocal-space Brillouin zone (BZ) integration does not scale as the cluster size increases like it would for say a supercell calculation. This feature also means the NLCPA can be used to investigate nonlocal disorder effects on Fermi surfaces [27] and transport properties e.g. resistivity in K-state alloys [28]. Another advantage of the NLCPA is that it is a self-consistent theory and is therefore able to give a self-consistent treatment of chemical SRO. This also means significant nonlocal effects such as large fractions of the Madelung energy in alloys can be captured using only small clusters, as will be shown later.

A brief outline of this highlight now follows. In order to explain the idea of the NLCPA as explicitly as possible, Section 2 first introduces the NLCPA in the context of a simple tight-binding model Hamiltonian. This enables a description of nonlocal correlations in the context of the disorder problem to be given in terms of the familiar Dyson equation involving the self-energy. The idea of the NLCPA as a systematic method for including these correlations is described and the computational algorithm of the method, which greatly aids an understanding of the formalism, is also detailed. Following this, a numerical investigation of the NLCPA is presented for a simple one-dimensional model in order to examine the validity of the method. In Section 3, following a brief introduction to KKR multiple scattering theory and a brief overview of the conventional SCF-KKR-CPA, the basic KKR-NLCPA formalism is outlined by making analogy with the tight-binding formalism of Section 2 where possible. The formalism presented here assumes the potentials have already been self-consistently determined using the SCF-KKR-CPA, so the calculations presented are 'first-pass' only in the sense that charge self-consistency with respect to the KKR-NLCPA medium itself is not enforced. Section 4 details the full charge self-consistent (SCF)-KKR-NLCPA formalism, including the expression for the total energy and a description of the charge-correlation (Madelung) term. An application to the $Cu_{50}Zn_{50}$ system is described, demonstrating the role of charge transfer and the variation of the total energy as a function of chemical SRO. Finally, conclusions are made and possible future work discussed in Section 5.

2 Tight-binding NLCPA

Nonlocal correlations

Consider a general tight-binding model Hamiltonian

$$H^{ij} = \epsilon^i \delta_{ij} + W^{ij}(1 - \delta_{ij}) \tag{1}$$

for a binary alloy defined by a hopping amplitude W^{ij} and site energies ϵ_A and ϵ_B. In terms of the site occupation numbers ξ_i which take on values of 0 and 1 depending on whether the site is occupied by an A-atom or a B-atom, the usual Green's function $G^{ij}(E)$ describing the propagation of an electron in the lattice satisfies the Dyson equation

$$G^{ij} = G_0^{ij} + \sum_k G_0^{ik} \epsilon^k G^{kj} \tag{2}$$

where $\epsilon_i = \xi_i \epsilon_A + (1 - \xi_i)\epsilon_B$ and G_0 is the free-particle Green's function. We are interested in $\langle G^{ij} \rangle$, the average of G^{ij} over all possible sets of disorder configurations $\{\xi_i\}$. By expanding (2) and averaging term by term, it is possible to express $\langle G^{ij} \rangle$ in the form

$$\langle G^{ij} \rangle = G_0^{ij} + \sum_{p,q} G_0^{ip} \Sigma^{pq} \langle G^{qj} \rangle \tag{3}$$

where Σ^{ij} is the exact self-energy. Here Σ^{ij} is a static nonlocal quantity associated with a configurational average over the disorder configurations. It is important to give a physical interpretation of (3). Since (3) is in the form of a Dyson equation, it may be interpreted as describing an electron propagating through an *effective medium* in which the site-diagonal part of Σ^{ij} decribes an effective on-site energy, and the site off-diagonal part describes an effective correction to the hopping. Significantly, since $\langle G^{ij} \rangle$ and correspondingly Σ^{ij} both possess the full translational symmetry of the underlying lattice, (3) may be expressed in reciprocal space as

$$\langle G(\mathbf{k}) \rangle = G_0(\mathbf{k}) + G_0(\mathbf{k})\Sigma(\mathbf{k}) \langle G(\mathbf{k}) \rangle = (E - W(\mathbf{k}) - \Sigma(\mathbf{k}))^{-1} \tag{4}$$

Then $\left\langle G^{ij}\right\rangle$ may be calculated via the BZ integral

$$\left\langle G^{ij}\right\rangle = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \left(E - W(\mathbf{k}) - \Sigma(\mathbf{k})\right)^{-1} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \tag{5}$$

from which observable properties can be calculated. In practice it is of course unfeasible to average over all possible configurations of an infinite (or very large) lattice. The aim of an effective medium theory is therefore to determine an approximation to the exact self-energy Σ^{ij} and corresponding $\left\langle G^{ij}\right\rangle$. The well-known CPA approach is to map the problem to that of a self-consistent single-site (local) impurity problem where one is only required to explicitly average over the possible configurations of a single site. The limitation of this approach is that all nonlocal physics is treated at mean-field level only. In other words, a site only feels the average effect of its environment and so nonlocal correlations in the disorder configurations are neglected. Therefore the CPA self-energy is a single-site quantity Σ^{ii} and has no dependence on momentum $\mathbf{k}$. A brief overview of the CPA now follows.

Conventional CPA

As mentioned above, the main approximation made by the CPA [1] is to assume a site-diagonal translationally-invariant self-energy $\Sigma^{ii}\delta_{ij}$. The CPA effective medium is then described by the equation

$$\overline{G}^{ij} = G_0^{ij} + \sum_k G_0^{ik}\Sigma^{kk}\overline{G}^{kj} \tag{6}$$

In order to determine the medium, let us consider any site i. By removing the sum over all sites k and making up for the neglected terms by replacing the free particle Green's function with the cavity Green's function $\mathcal{G}^{ii}$, the site-diagonal part of (6) at site i can be formally rewritten in the form

$$\overline{G}^{ii} = \mathcal{G}^{ii} + \mathcal{G}^{ii}\,\Sigma^{ii}\,\overline{G}^{ii} = \left(\left(\mathcal{G}^{ii}\right)^{-1} - \Sigma^{ii}\right)^{-1} \tag{7}$$

where $\mathcal{G}^{ii}$ can be written in terms of an expansion over the remaining lattice sites. It can be seen that $\mathcal{G}^{ii}$ depends only on the medium surrounding site i and is independent of the chemical occupation of i itself. It is therefore straightforward to define the Green's function for a real *impurity* embedded in the medium simply by replacing the effective site energy Σ^{ii} with a real site energy ϵ_α^i at site i, where $\alpha = A$ or B. From (7) this is given by

$$G_\alpha^{ii} = \left(\left(\mathcal{G}^{ii}\right)^{-1} - \epsilon_\alpha^i\right)^{-1} = \left(\Sigma^{ii} - \epsilon_\alpha^i + (\overline{G}^{ii})^{-1}\right)^{-1} \tag{8}$$

Now the CPA demands that

$$\sum_\alpha P_\alpha G_\alpha^{ii} = \overline{G}^{ii} \tag{9}$$

where P_α is the probability that site i is of chemical type α. In other words, the replacement of an effective site energy by a real site energy should, on the average, produce no change to the CPA medium. Since the medium is translationally-invariant, it follows from (6) that $\overline{G}^{ii}$ must also satisfy the BZ integral

$$\overline{G}^{ii} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\mathbf{k}\,\left(E - \Sigma^{(ii)} - W(\mathbf{k})\right)^{-1} \tag{10}$$

The CPA medium is therefore determined from a self-consistent solution of (9) and (10).

Idea of the NLCPA

In order to go beyond the CPA and include nonlocal correlations in the disorder configurations, it is clear that we need to generalise the single-site CPA approach and average over an ensemble of impurity *cluster* configurations. This would enable us to define a cluster self-energy Σ^{IJ}, where $\{I, J\}$ are cluster sites. In brief, knowledge of correlated hoppings for specific cluster disorder configurations means the intra-cluster hopping would be modified on the average and therefore the self-energy would gain an off-diagonal part. Although such a generalisation appears straightforward, the main difficulty is in preserving translational invariance and formulating a consistent treatment in reciprocal space, for example treating a site at say the boundary of the cluster in an identical manner as say a site at the centre of the cluster. The NLCPA solves the problem of maintaining translational invariance by *imposing Born-von Karman boundary conditions on the cluster*. The idea is to self-consistently embed a cluster (or finite-sized lattice) with Born-von Karman boundary conditions into an infinite lattice with Born-von Karman boundary conditions. The extent of nonlocal correlations included in the resulting effective medium are limited by the size of the cluster, however all symmetries of the underlying lattice are preserved.

Cluster with Born-von Karman boundary conditions

The first step in the derivation of the NLCPA is to solve the problem of a cluster with Born-von Karman (periodic) boundary conditions. This essentially means reducing the size of a conventional lattice with Born-von Karman boundary conditions to contain only a cluster of N_c sites, so that the edges of the cluster map round to the other end along each axis. Since the lattice constant is unchanged, the boundaries of the BZ will remain the same, however it will now contain only N_c evenly spaced $\mathbf{k}$ points referred to as the set of *cluster momenta* $\{\mathbf{K}_n\}$ [15], where $n = 1, .., N_c$. Therefore the conventional lattice Fourier transform used in the $N_c \to \infty$ limit reduces to the cluster Fourier transform

$$\frac{1}{N_c} \sum_{\mathbf{K}_n} e^{i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} = \delta_{IJ} \tag{11}$$

which relates the real-space cluster sites $\{I\}$ (denoted by capital letters) to the corresponding set of cluster momenta $\{\mathbf{K}_n\}$ [15]. Significantly, averaged cluster quantities are now translationally-invariant and can be related in real and reciprocal space through (11), for example for the cluster self-energy we have

$$\Sigma_{cl}^{IJ} = \frac{1}{N_c} \sum_{\mathbf{K}_n} \Sigma_{cl}(\mathbf{K}_n) e^{i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} \quad \text{and} \quad \Sigma_{cl}(\mathbf{K}_n) = \sum_J \Sigma_{cl}^{IJ} e^{-i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} \tag{12}$$

However, there are restrictions on the possible choices of cluster that may be used when mapping the cluster to the lattice. As explained in Ref. [15], it must be possible to surround the cluster sites with a space-filling tile, the principal axes of which must point along a high symmetry direction of the underlying lattice. An example cluster and tile for a square lattice in 2D with $N_c = 4$ is shown in Fig. 1(a). Note that in a supercell calculation, this real space tile would correspond to a reciprocal space tile centred at one of the points $\{\mathbf{K}_n\}$, which would be the new (smaller) BZ. However, the NLCPA is not a supercell calculation and the idea is to use N_c such tiles centred at each of the cluster momenta $\{\mathbf{K}_n\}$ to fill out the original BZ of the underlying lattice, thus preserving translational invariance. This is shown for the same example as above in Fig. 1(b). Importantly, the shape and size of the real space tile surrounding the cluster sites corresponds to the shape and size of the reciprocal space tiles surrounding the cluster momenta.

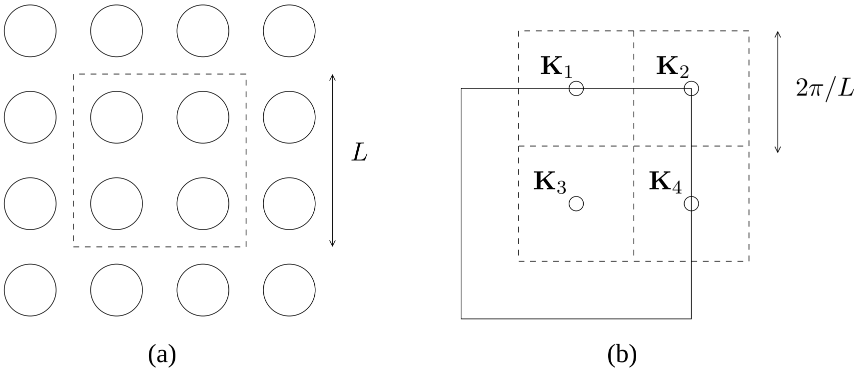


Figure 1: (a) Real-space tile for a 2D square lattice with cluster size $N_c = 4$. The linear length of the tile is $L = 2a$ where a is the lattice constant. (b) Corresponding reciprocal-space tiles centred at the (periodic) cluster momenta $\{\mathbf{K}_n\}$. The solid line denotes the 1st BZ. Note that parts of tiles lying outside the 1st BZ can be translated through reciprocal lattice vectors to lie inside the 1st BZ.

Mapping cluster to lattice

In order to self-consistently determine the medium, we first need to map the cluster problem to the lattice problem in reciprocal space. Here it is important to distinguish between cluster and lattice quantities. The exact lattice self-energy $\Sigma(\mathbf{k})$ given in (4) is the unknown quantity which we wish to approximate. However, let us assume at this stage that we do know a cluster self-energy $\Sigma_{cl}(\mathbf{K}_n)$ (this will in fact be determined later when solving the impurity problem).

The first step in the mapping is to average $\Sigma(\mathbf{k})$ over the momenta $\mathbf{q}$ within each of the N_c tiles, such as those shown in Fig. 1. This results in a *coarse-grained* lattice self-energy $\Sigma(\mathbf{K}_n)$ which has a constant but different value within each tile. On the other hand, the cluster self-energy $\Sigma_{cl}(\mathbf{K}_n)$ is defined only at the cluster momenta $\{\mathbf{K}_n\}$. The main approximation made by the NLCPA [15] is to set $\Sigma(\mathbf{K}_n)$ to be equal to the value $\Sigma_{cl}(\mathbf{K}_n)$ within each tile n i.e.

$$\frac{1}{\Omega_{\mathbf{K}_n}} \int_{\Omega_{\mathbf{K}_n}} d\mathbf{q}\, \Sigma(\mathbf{K}_n + \mathbf{q}) = \Sigma(\mathbf{K}_n) \simeq \Sigma_{cl}(\mathbf{K}_n) \tag{13}$$

In other words, the lattice self-energy is approximated by that obtained from the cluster. Physically, this means that the exact medium described by (4) has been replaced by an effective medium which is still translationally-invariant but the range of nonlocal correlations retained are restricted by the size of the cluster. Note that a precise correlation length can be defined using Nyquist's sampling theorem [15, 29].

The lattice Green's function in reciprocal space may be represented by summing over the dispersion within each tile, yielding the set of coarse-grained values

$$\overline{G}(\mathbf{K}_n) = \frac{N_c}{\Omega_{BZ}} \int_{\Omega_{\mathbf{K}_n}} d\mathbf{k}\, (E - W(\mathbf{k}) - \Sigma(\mathbf{K}_n))^{-1} \tag{14}$$

which are straightforward to calculate since $\Sigma(\mathbf{K}_n)$ is constant within each tile $\Omega_{\mathbf{K}_n}$. This step is consistent with the approximation made above and is carried out to remove phase factors involving lattice momenta. The real space Green's function at the cluster sites can now be obtained using (11) i.e.

$$\overline{G}^{IJ} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \int_{\Omega_{\mathbf{K}_n}} d\mathbf{k}\, (E - W(\mathbf{k}) - \Sigma(\mathbf{K}_n))^{-1}\, e^{i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} \tag{15}$$

Impurity problem

At this stage, we have assumed that the cluster self-energy is known. However, in order to determine a cluster self-energy, the impurity problem must be solved. The first step is to define the reciprocal space cavity Green's function $\mathcal{G}(\mathbf{K}_n)$ via the Dyson equation

$$\overline{G}(\mathbf{K}_n) = \mathcal{G}(\mathbf{K}_n) + \mathcal{G}(\mathbf{K}_n)\Sigma(\mathbf{K}_n)\overline{G}(\mathbf{K}_n) \tag{16}$$

In diagrammatic terms $\mathcal{G}(\mathbf{K}_n)$ is introduced to avoid over-counting self-energy diagrams on the cluster [16]. Equation (16) can also be expressed in real space by applying the Fourier transform (11) to yield

$$\overline{G}^{IJ} = \mathcal{G}^{IJ} + \sum_{K,L} \mathcal{G}^{IK}\Sigma^{KL}\overline{G}^{LJ} \tag{17}$$

where $\mathcal{G}^{IJ}$ is the real space cavity Green's function. Significantly, $\mathcal{G}^{IJ}$ is independent of the chemical occupation of the cluster itself. This means the NLCPA impurity cluster Green's function may be defined simply by replacing the cluster self-energy in (17) with a particular configuration of site energies $\{\epsilon^I_\alpha\}$ i.e.

$$G^{IJ}_\gamma = \mathcal{G}^{IJ} + \sum_{K} \mathcal{G}^{IK}\epsilon^K_\alpha G^{KJ}_\gamma \tag{18}$$

The NLCPA self-consistency condition is

$$\sum_\gamma P_\gamma G^{IJ}_\gamma = \overline{G}^{IJ} \tag{19}$$

where P_γ is the probability of configuration γ occuring (weighted to include SRO if desired). It is important to realise that (19) is the step which implicitly generates the cluster self-energy. The effective medium is therefore determined from a self-consistent solution of (15) and (19). Finally note that the NLCPA formalism reduces to the CPA for $N_c = 1$ and becomes exact as $N_c \to \infty$ since this would amount to solving the exact problem described by (3) and (4).

Algorithm

In the following, an underscore denotes a matrix in the cluster-site index. For each energy E,

1. For the first iteration, make a guess for the cluster self-energy $\underline{\Sigma}$ e.g. zero.
2. Convert the matrix elements Σ^{IJ} to reciprocal space using (11).
3. Calculate the matrix elements $\overline{G}(\mathbf{K}_n)$ using (14) and convert to real space using (11).
4. Calculate the cavity Green's function by solving (17) i.e. $\underline{\mathcal{G}} = \left(\underline{\overline{G}}^{-1} + \underline{\Sigma}\right)^{-1}$.
5. Calculate the impurity Green's function for each of the 2^{N_c} impurity cluster configurations via (18).
6. Calculate a new $\underline{\overline{G}}$ by averaging $\underline{G}_\gamma$ over all configurations (with an appropriate weighting to include SRO if required).

7. Using $\underline{\mathcal{G}}$ from step 4 and the new $\underline{\overline{G}}$ from step 6, calculate a new guess at the self-energy via $\underline{\Sigma} = \underline{\mathcal{G}}^{-1} - \underline{\overline{G}}^{-1}$.

8. Compare the new matrix elements Σ^{IJ} with those in step 1. If they are not equal to within the desired accuracy, repeat as necessary steps 2 → 8 using the new $\underline{\Sigma}$ until convergence within the desired accuracy is achieved.

Calculating observables

Once the medium has been determined through (15) and (19), there is no longer any need to coarse-grain the Green's function via (14). Now, the Green's function may be calculated at any point in the BZ through

$$\overline{G}(\mathbf{k}) = (E - W(\mathbf{k}) - \Sigma(\mathbf{K}_n))^{-1} \tag{20}$$

and correspondingly at any sites i, j in the lattice by

$$\overline{G}^{ij} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\mathbf{k}\, (E - W(\mathbf{k}) - \Sigma(\mathbf{K}_n))^{-1} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \tag{21}$$

In (20) and (21) above, $\Sigma(\mathbf{K}_n)$ takes the appropriate value within each tile n. The configurationally-averaged DOS per site is given by the usual expression

$$\overline{n}(E) = -\frac{1}{\pi} Im\, \overline{G}^{II} \tag{22}$$

where $\overline{G}^{II}$ is independent of the choice of site I. However, when calculating site-off diagonal observables such as the spectral function, notice that $\Sigma(\mathbf{K}_n)$ taking the appropriate constant value within each tile in (20) leads to unphysical discontinuities in $\overline{G}(\mathbf{k})$ at the tile boundaries. This point will be addressed and resolved in the following numerical investigation.

Numerical Investigation

Due to the numerous possible applications and further conceptual development of the NLCPA method, it is important to carry out a numerical investigation in order to establish that the theory produces physically meaningful results. For example, imposing Born-von Karman boundary conditions on the cluster could introduce fluctuations that have no physical relation to the real system. If it is found that the fluctuations are real, it should then be checked that bulk quantities converge towards the exact result as the cluster sizes increases, and whether this convergence is systematic. In order to answer such questions, a numerical investigation of the NLCPA was recently carried out in [30] for a simple 1D model Hamiltonian with random diagonal disorder and nearest neighbour hopping. This is because in 1D the exact result can be obtained numerically, for example using the negative eigenvalue theorem [31]. Also, fluctuations are much more significant in 1D and so detailed structure is expected in the density of states (DOS) which can be accurately compared with both the exact result and other cluster theories such as the embedded cluster method (ECM) [14] and molecular coherent-potential approximation (MCPA) [32,33]. The MCPA is essentially a self-consistent averaged-supercell calculation and is not computationally feasible for realistic systems, however it should yield meaningful results here for the DOS. The ECM is a non-self-consistent cluster theory, however we would also expect the ECM results to be very similar to

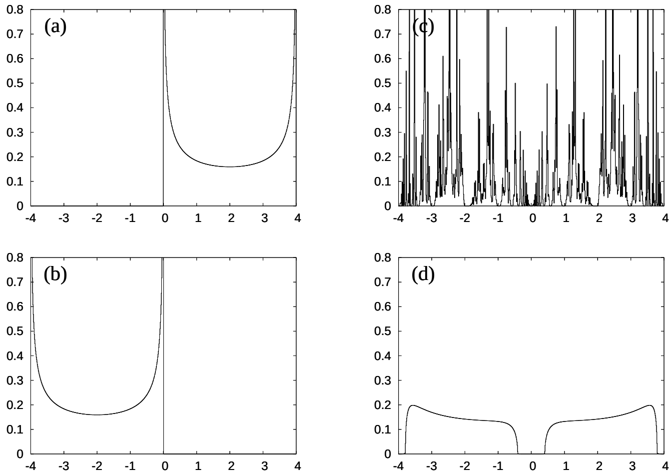


Figure 2: (a) DOS (as a function of energy) for a pure material comprising of A sites, with $\epsilon_A = +2.0$. (b) DOS for a pure material comprising of B sites, with $\epsilon_B = -2.0$. (c) Exact DOS results for a random $A_{50}B_{50}$ alloy of the pure materials above. (d) DOS for the same $A_{50}B_{50}$ alloy obtained using the CPA.

the NLCPA in the absence of chemical short-range order (SRO) since the effects of self-consistency are less significant in the random case.

In summary, it was found in [30] that the NLCPA does produce physically meaningful results, but only above some critical cluster size. To illustrate this, Fig. 2 shows the exact DOS plot for a random (i.e. no SRO) $A_{50}B_{50}$ alloy of constituent site energies $\epsilon_A = +2.0$ and $\epsilon_B = -2.0$ with hopping parameter $W = 1.0$, together with the conventional CPA result. Fig. 3 and Fig. 4 show results for the same model obtained using the ECM (first row), MCPA measured on central site (second row), MCPA averaged over all cluster sites (third row), and the NLCPA with periodic Born-von Karman boundary conditions (fourth row), all as a function of cluster size. It is clear that in the NLCPA calculations for small clusters, there are features present that are not seen elsewhere and appear to be unphysical (for example the troughs present at $E = -3$ and $E = -1.5$ in the $N_c = 2$ calculation). However, such unphysical features are not present for larger cluster sizes and it can be seen that the NLCPA does indeed then converge systematically towards the exact result (note that the ECM converges more quickly here only due to the absence of SRO). However, the apparent unphysical nature of the results for small clusters is an unsatisfactory situation and some solution to the problem is needed.

In order to investigate this problem, calculations were performed in [30] using *anti-periodic* [17] Born-von Karman boundary conditions applied to the cluster instead of the conventional periodic conditions (i.e. quantities at the edges of the cluster map round to minus the value at the opposite edges along each axis). For an infinite cluster, the periodic and anti-periodic sets of cluster momenta ($\{\mathbf{K}_P\}$ and $\{\mathbf{K}_{AP}\}$ respectively) are equivalent, however as the cluster size decreases, the $\{\mathbf{K}_{AP}\}$ are shifted compared to $\{\mathbf{K}_P\}$ and lie symmetric about the origin (see Fig. 5) for a 1D example with $N_c = 4$). Results obtained using $\{\mathbf{K}_{AP}\}$ are shown in the fifth row of Fig. 3 and Fig. 4. It can be seen that below a critical cluster size (here $N_c = 12$) the periodic and anti-periodic results diverge and gain unphysical features, although both become equivalent and equal the CPA result at $N_c = 1$. This suggests that when using the NLCPA for cluster sizes $1 < N_c < N_{critical}$, a way forward is to appropriately mix the periodic and anti-periodic results to produce a new unique solution.

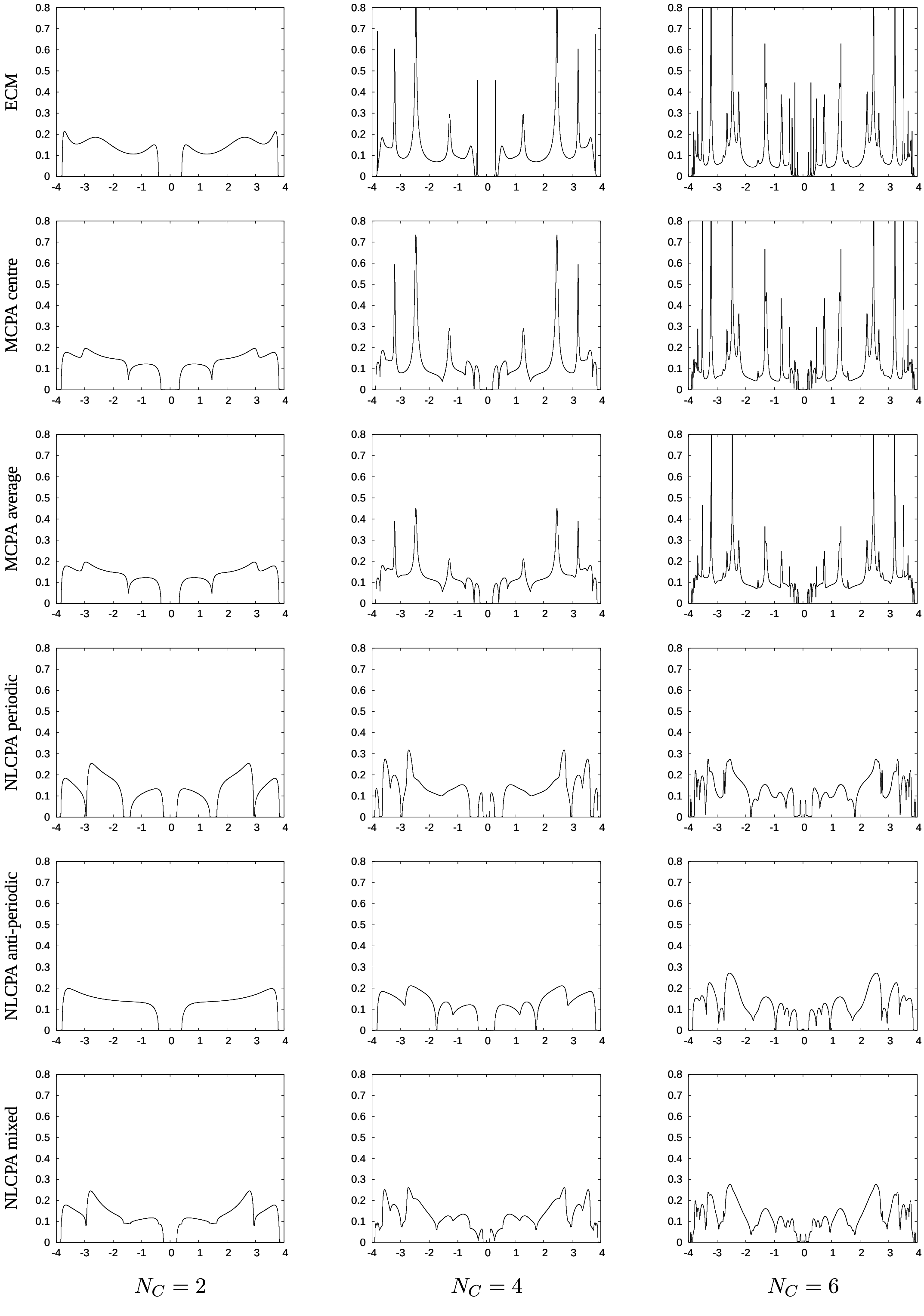
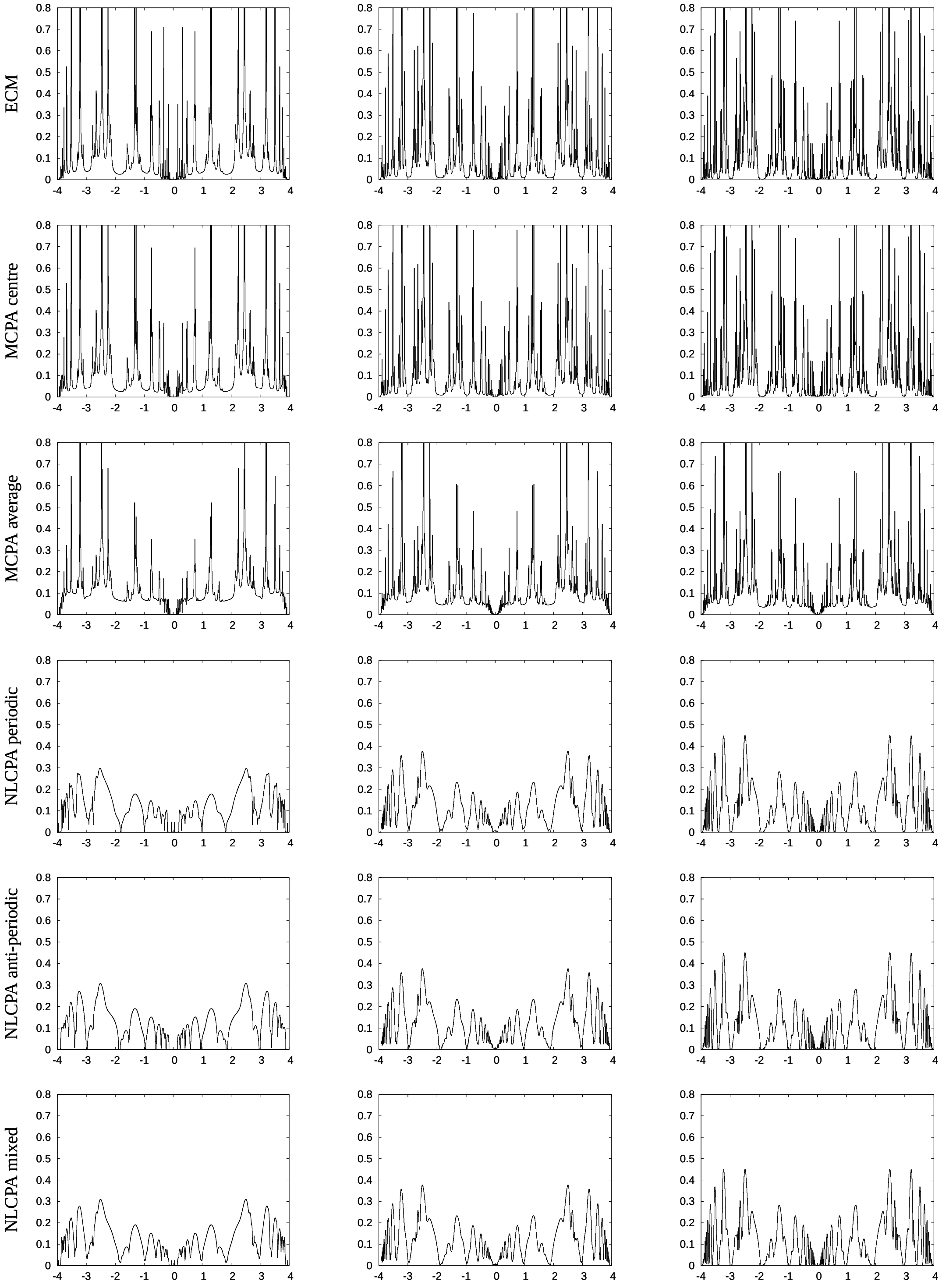


Figure 3: Configurationally-averaged DOS per site as a function of energy (in units of the bandwidth) for the various cluster theories (top to bottom) with cluster sizes $N_c = 2, 4, 6$ (left to right).



$N_C = 8$ $N_C = 12$ $N_C = 16$

Figure 4: Configurationally-averaged DOS per site as a function of energy (in units of the bandwidth) for the various cluster theories (top to bottom) with cluster sizes $N_c = 8, 12, 16$ (left to right).

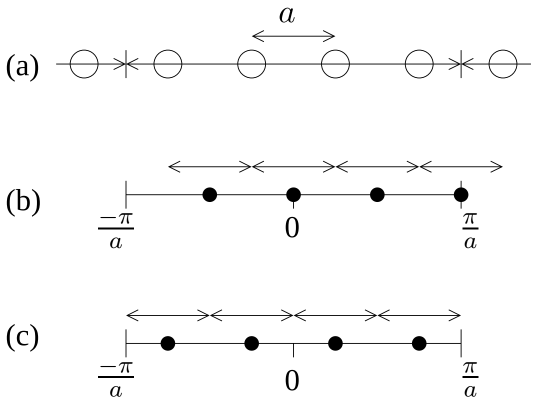


Figure 5: (a) Real space tile (denoted by double-headed arrow of length $4a$) for a $N_c = 4$ cluster in 1D. Sites are denoted by open circles, and a is the lattice constant. (b) Set of cluster momenta (periodic) denoted by closed circles for the $N_c = 4$ cluster. The tiles centred at the cluster momenta are denoted by arrows and the solid line is the first BZ. The part of the tile centred at π/a that lies outside the first BZ can be translated by reciprocal lattice vectors into the first BZ to lie between $-\pi/a$ and $-\pi/4a$. (c) Set of cluster momenta (anti-periodic) denoted by closed circles for the $N_c = 4$ cluster. Again the tiles centred at the cluster momenta are denoted by arrows and the solid line is the first BZ.

Let us begin by labelling the Green's function (given by (20)) for the periodic and anti-periodic solutions by $\overline{G}_P(\mathbf{k})$ and $\overline{G}_{AP}(\mathbf{k})$ respectively. Next, observe that on account of the coarse-graining procedure outlined earlier, by construction $\overline{G}_P(\mathbf{k})$ is a better approximation to the exact result in the region of reciprocal space close to each of the points $\{\mathbf{K}_n^P\}$ (in fact $\overline{G}_{AP}(\mathbf{k})$ has discontinuities at $\{\mathbf{K}_n^P\}$). Similarly $\overline{G}_{AP}(\mathbf{k})$ is a better approximation to the exact result close to each of the points $\{\mathbf{K}_n^{AP}\}$. This suggests that one should construct a new mixed Green's function $\overline{G}_M(\mathbf{k})$ which follows $\overline{G}_P(\mathbf{k})$ close to each of the points $\{\mathbf{K}_n^P\}$, and follows $\overline{G}_{AP}(\mathbf{k})$ close to each of the points $\{\mathbf{K}_n^{AP}\}$. A method for carrying out this has been proposed in [34]. By defining a mixing parameter which is subject to conditions at the tile boundaries, such a problem can be directly mapped to that of the potential of a static membrane, the minimization of which gives the well known Laplace equation describing wave motion. For example, in 1D this yields the simple expression

$$\overline{G}_M(\mathbf{k}) = \overline{G}_P(\mathbf{k}) \cos^2\left((N_c a/2)\mathbf{k}\right) + \overline{G}_{AP}(\mathbf{k}) \sin^2\left((N_c a/2)\mathbf{k}\right) \tag{23}$$

for the new mixed Green's function. The final row in Fig. 3 and Fig. 4 show DOS results using (23). Reassuringly, the new mixed NLCPA result looks remarkably similar to both the ECM and MCPA results for all cluster sizes, with unphysical features removed and troughs and peaks in the DOS which can be associated with specific cluster disorder configurations.

In conclusion, when using the NLCPA one should first establish the critical cluster size $N_{critical}$ for the model in question i.e. the smallest cluster for which the periodic and anti-periodic results are equivalent. For $N_c \geq N_{critical}$ the result is independent of the boundary condition and thus the conventional periodic results may be used. For calculations with $1 < N_c < N_{critical}$, the method proposed in [34] should be used to mix the periodic and anti-periodic results. Note that the method is perfectly general and can be applied to any (allowed) cluster in any dimension.

Spectral function in the NLCPA

The success of the method of [34] mentioned above for mixing the periodic and anti-periodic solutions is due to the fact that in addition to effectively increasing the number of cluster momenta in the BZ (see Fig. 5), it removes the problem of discontinuities in the self-energy and Green's function since no individual solution is followed where it has a discontinuity. Therefore the mixed Green's function $\overline{G}_M(\mathbf{k})$ has its own associated self-energy which is fully $\mathbf{k}$-dependent and continuous. In addition to yielding unique, meaningful, and systematic results, the method therefore also yields a well-defined spectral function

$$A_B^M(\mathbf{k},\epsilon) = -\frac{1}{\pi} Im\,\overline{G}_M(\mathbf{k},\epsilon) \tag{24}$$

which can be used to calculate Fermi surfaces. Some spectacular new Fermi surface features obtained using the method (such as new nesting features and an electronic topological transition not predicted by the conventional CPA) are illustrated in [34] for a 2D tight-binding model. Clearly, it would be beneficial to apply the method within first-principles KKR calculations. A derivation and implementation of the spectral function has recently been given within the first-principles KKR-NLCPA multiple-scattering theory in [35], although only the periodic set of cluster momenta are used and no attempt is made to remove the discontinuities. The formalism of [35] combined with that of [34] would enable the effects of SRO to be studied on interesting Fermi surface features of systems such as $CuPd$ [27].

3 KKR-NLCPA

Brief introduction to KKR theory

The aim of a first-principles electronic structure method is to solve the Kohn-Sham equation. Instead of calculating the charge density from the single-electron Kohn-Sham states, the KKR method uses the corresponding single-electron multiple-scattering Green's function. To do this, the usual Dyson equation in operator form $(G = G_0 + G_0 V G)$ is rewritten as

$$G = G_0 + G_0 T G_0 \tag{25}$$

where the multiple scattering T operator has been defined by $VG = TG_0$ and describes all possible scattering in the system as it relates the free-particle Green's operator to the full scattering Green's operator. The basic idea is to represent the multiple-scattering problem in terms of the scattering properties of the individual sites. By decomposing the effective Kohn-Sham potential into contributions from individual sites, it can be shown that the transition operator T can be written in terms of the multiple scattering operator τ^{ij} by $T = \sum_{ij} \tau^{ij}$ where

$$\tau^{ij} = t^i \delta_{ij} + \sum_{k\neq i} t^i G_0^{ik} t^k \delta_{kj} + \sum_{k\neq i}\sum_{l\neq k} t^i G_0^{ik} t^k G_0^{kl} t^l \delta_{lj} + \cdots = t^i \delta_{ij} + \sum_{k\neq i} t^i G_0^{ik} \tau^{kj} \tag{26}$$

Here the single-site t-operators describe the scattering at each individual site and G_0 the free-space propagation of an electron in between scattering events. So τ^{ij} gives the scattered wave from site i due to a wave incident upon site j, taking into account all possible scatterings in between.

For computational purposes, we need to go into a coordinate and angular momentum representation. In a coordinate representation, the effective potential $V(\mathbf{r})$ is taken as a sum of non-overlapping spherical contributions $V_i(\mathbf{r} - \mathbf{R}_i)$ centred at each site $\mathbf{R}_i$, and is set equal to zero or a constant in the interstitial region outside these 'muffin-tin' spheres. Then by performing a partial wave decomposition, (25) and (26) eventually become

$$G(\mathbf{r}, \mathbf{r}', E) = \sum_L Z_L(\mathbf{r}_i, E)\tau^{ij}_{LL'}(E)Z_{L'}(\mathbf{r}'_j, E) - \delta_{ij}\sum_L Z_L(\mathbf{r}^<_i, E)\tilde{J}_L(\mathbf{r}^>_i, E) \tag{27}$$

$$\tau^{ij}_{LL'}(E) = t^i_L(E)\delta_{ij}\delta_{LL'} + \sum_{k\neq i}\sum_{L''} t^i_L(E)G_{0,LL''}(\mathbf{R}_i - \mathbf{R}_k, E)\tau^{kj}_{L''L'}(E) \tag{28}$$

respectively, where $\mathbf{r} = \mathbf{r}_i + \mathbf{R}_i$ is restricted to lie in the i^{th} bounding sphere and $\mathbf{r}' = \mathbf{r}'_j + \mathbf{R}_j$ in the j^{th} sphere, and $L = \{l, m\}$ is the angular momentum index. The free-space structure constants $G_{0,LL''}(\mathbf{R}_i - \mathbf{R}_k, E)$ describing the free-particle propagation in between scattering events depend on the structure of the lattice only. $Z_L(\mathbf{r}_i, E)$ is the solution of the single-site Schrödinger equation at site i that is regular at the origin and must join smoothly to a linear combination of free-particle solutions at the muffin-tin boundary. Using the normalisation of Ref. [36], this combination is taken to be

$$Z_L(\mathbf{r}, E) = J_L(\mathbf{r}, E)t^{-1}_L(E) - ikH_L(\mathbf{r}, E) \tag{29}$$

where $k = \sqrt{2mE/\hbar^2}$, $J_L(\mathbf{r}, E) = j_l(r, E)Y^m_l(\widehat{r})$, and $H_L(\mathbf{r}, E) = h_l(r, E)Y^m_l(\widehat{r})$. In (27), $\tilde{J}_L(\mathbf{r}, E)$ is the solution of the single-site Schrödinger equation at site i that is irregular at the origin and must join must join smoothly to the free particle solution $J_L(\mathbf{r}, E)$ at the muffin-tin boundary. Equation (29) also defines the single-site t-matrix, which is related to the phase shift by

$$t_L(E) = -\frac{1}{\sqrt{E}}\sin\delta_L(E)e^{i\delta_L} \tag{30}$$

For clarity, (28) may be written in the form

$$\underline{\tau}^{ij} = \underline{t}^i\delta_{ij} + \sum_{k\neq i}\underline{t}^i\underline{G}(\mathbf{R}_{ik})\underline{\tau}^{kj} \tag{31}$$

where the underscore denotes a matrix in the angular momentum index (usually cut off at $L = 2$ or 3). For translationally-invariant systems (31) may be expressed in reciprocal space as

$$\underline{\tau}(\mathbf{k}) = \underline{t} + \underline{t}\,\underline{G}(\mathbf{k})\,\underline{\tau}(\mathbf{k}) = \left(\underline{t}^{-1} - \underline{G}(\mathbf{k})\right)^{-1} \tag{32}$$

Therefore once the t-matrix and structure constants are known, the matrix elements $\underline{\tau}^{ij}$ may be calculated via the BZ integral

$$\underline{\tau}^{ij} = \frac{1}{\Omega_{BZ}}\int d\mathbf{k}\left(\underline{t}^{-1} - \underline{G}(\mathbf{k})\right)^{-1}e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \tag{33}$$

The Green's function may then be calculated via (27) from which observables can be found. For example, the charge density is given by

$$\rho(\mathbf{r}) = -\frac{1}{\pi}Im\int_{-\infty}^{E_F} G(\mathbf{r}, \mathbf{r}, E)dE \tag{34}$$

for reconstructing the effective potential $V(\mathbf{r})$ in the DFT self-consistency loop.

Self-Consistent-Field (SCF)-KKR-CPA

In principle, a DFT calculation for a disordered system means that self-consistency with respect to the electronic charge distribution should be achieved for each disorder configuration individually and then an average taken over all disorder configurations. This is clearly intractable, and so the strategy behind the SCF-KKR-CPA [8,9] is to enforce charge self-consistency only with respect to single-site *partially-averaged* charge densities ρ_α, such single-site partial averages being the constrained average over all configurations which leave the occupancy of a single site of chemical type α fixed [8,9]. The Kohn-Sham effective potential V_α is taken to depend only on ρ_α on the fixed site and the average charge density $\sum_\alpha \rho_\alpha$ on all other sites. So for a binary alloy, self-consistency is achieved when the partially-averaged charge densities ρ_A and ρ_B are consistent with the effective potentials V_A and V_B. Note that the total energy is expressed as a functional of the $\{\rho_\alpha\}$ and is stationary with respect to them [11], which is one of the main reasons behind the success of the method.

Let us assume that we are given two output effective potentials V_A and V_B. From these, we can calculate the single-site t-matrices $\underline{t}_A$ and $\underline{t}_B$. The KKR-CPA must now be used to perform the configurational averaging. To do this, we proceed in analogy to the derivation of the CPA within the tight-binding framework in Section 2. The KKR-CPA assumes a translationally-invariant effective medium comprising of identical effective scatterers $\underline{\bar{t}}$ placed on every site. The effective scattering path matrix $\underline{\bar{\tau}}^{ij}$ describing such a medium is given by

$$\underline{\bar{\tau}}^{ij} = \underline{\bar{t}}^{i}\,\delta_{ij} + \sum_{k\neq i} \underline{\bar{t}}^{i}\,\underline{G}(\mathbf{R}_{ik})\underline{\bar{\tau}}^{kj} \tag{35}$$

In order to determine the medium, consider a site i. By removing the sum over all sites k and making up for the neglected terms by introducing the renormalised interactor $\underline{\bar{\Delta}}^{ii}$, the site-diagonal part of (35) at site i can be formally rewritten in the form

$$\underline{\bar{\tau}}^{ii} = \underline{\bar{t}}^{i}\,\delta_{ij} + \underline{\bar{t}}^{i}\,\underline{\bar{\Delta}}^{ii}\underline{\bar{\tau}}^{ii} \;=\; \left(\underline{\bar{t}}^{i^{-1}} - \underline{\bar{\Delta}}^{ii}\right)^{-1} \tag{36}$$

where the renormalised interactor $\underline{\bar{\Delta}}^{ii}$ can be written in terms of an expansion over the remaining lattice sites [14]. Since $\underline{\bar{\Delta}}^{ii}$ describes the interaction of site i with the rest of the medium i.e. describes all paths starting and ending on site i which avoid site i at all intermediate steps, it is independent of the nature of the potential at site i. It is therefore straightforward to define the path matrix for paths starting and ending on a real *impurity* embedded in the medium simply by replacing the effective scatterer $\underline{\bar{t}}$ with a real t-matrix $\underline{t}^{i}_{\alpha}$ at site i, where $\alpha = A$ or B. From (36) this is given by

$$\underline{\tau}^{ii}_{\alpha} = \left(\underline{t}^{i\;-1}_{\alpha} - \underline{\bar{\Delta}}^{ii}\right)^{-1} = \left[\underline{\bar{\tau}}^{ii^{-1}} + \underline{t}^{i\;-1}_{\alpha} - \underline{\bar{t}}^{i^{-1}}\right]^{-1} \tag{37}$$

The KKR-CPA requires that

$$\sum_\alpha P_\alpha \underline{\tau}^{ii}_{\alpha} = \underline{\bar{\tau}}^{ii} \tag{38}$$

where P_α is the probability that site i is of chemical type α. In other words, there should be no excess scattering from the impurity site on the average. Since we require the KKR-CPA effective medium to be translationally-invariant, $\underline{\bar{\tau}}^{ii}$ must also satisfy the BZ integral

$$\underline{\bar{\tau}}^{ii} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\mathbf{k}\left(\underline{\bar{t}}^{-1} - G(\mathbf{k})\right)^{-1} \tag{39}$$

The KKR-CPA medium is therefore determined from a self-consistent solution of (38) and (39). After the medium has been determined, the site-diagonal part of the Green's function (27) for an impurity site embedded in the medium is given by

$$G_\alpha(E,\mathbf{r}_i,\mathbf{r}'_i) = \sum_{LL'} P_\alpha Z^\alpha_L(E,\mathbf{r}_i)\tau^{ii}_{\alpha,LL'} Z^i_{L'}(E,\mathbf{r}'_i) - \sum_L P_\alpha Z^\alpha_L(E,\mathbf{r}_i)\tilde{J}^\alpha_L(E,\mathbf{r}'_i) \tag{40}$$

where α denotes a site of type A or B, and $\tau^{ii}_{\alpha,LL'}$ is given by (37). The total average Green's function is then given by summing over α. However, from (40) we can calculate the charge density at the impurity site via

$$\rho_\alpha(\mathbf{r}_i) = -\frac{1}{\pi} Im \int_{-\infty}^{E_F} G_\alpha(E,\mathbf{r}_i,\mathbf{r}_i)dE \tag{41}$$

This is the CPA approximation to the single-site partially-averaged charge density since it is the charge density for a fixed site embedded in a (mean-field) averaged environment. Using ρ_α on the fixed site and the average charge density $\sum_\alpha \rho_\alpha$ on all other sites, new effective potentials $\{V_\alpha\}$ can be contructed for feeding back to the DFT self-consistency loop [8, 9].

‘First-Pass’ KKR-NLCPA

The key step in deriving the NLCPA within the KKR multiple scattering framework is to identify the quantities which played the role of the self-energy Σ^{ij} in the derivation within the tight-binding framework in Section 2. It is clear that there is a direct analogy between the single-site t-matrices $\underline{t}^i$ and the site energies ϵ^i, and similarly between the free-space structure constants $\underline{G}(\mathbf{R}_{ij})$ and the hopping terms W^{ij}. This implies that for the site-diagonal part of Σ^{ij}, which describes an effective on-site energy, there is a clear analogy to an effective single-site t-matrix $\underline{\widehat{t}}^i$. For the site off-diagonal part of Σ^{ij}, which from (4) describes an effective correction to the hopping, it follows that we need to introduce a new effective correction $\underline{\widehat{\delta G}}(\mathbf{R}_{ij})$ to the free-space structure constants $\underline{G}(\mathbf{R}_{ij})$. Of course, in the conventional KKR-CPA theory such corrections are never present since the ‘coherent-potential’ is a single-site quantity, analogous to a single-site self-energy Σ^{ii} only within the tight-binding framework.

However, there are important differences in the physical interpretation of the above quantities. Recall that one of the main advantages of the multiple scattering formalism (which for disordered systems facilitates its combination with DFT) is that there is a complete separation between the potential and structural information. The free-space structure constants contain information about the structure of the lattice only; all potential information is contained within the single-site t-matrices. This means that the new effective structure constant corrections $\underline{\widehat{\delta G}}(\mathbf{R}_{ij})$ are limited to describing nonlocal *scattering correlations* only. In other words, in between scattering events, an electron now propagates though a reference medium which is no longer free space. This medium takes into account, on average, the effect on the propagation of the electron due to multiple scatterings from specific disorder configurations. Note that such scattering correlations are present even in the absence of chemical SRO.

Nonlocal *charge correlations* which arise due to the transfer of charge between sites of differing atomic species can be taken into account by combination with DFT i.e. when the potentials are self-consistently determined. Possible charge transfer will then manifest itself by changes to the t-matrices which are fed to the KKR-NLCPA. However, the treatment of charge correlations will not be considered in this section. Here we will simply assume that we have two t-matrices $\underline{t}_A$ and $\underline{t}_B$, for example corresponding to potentials that have been determined self-consistently by the SCF-KKR-CPA described above. The aim is therefore only to do a ‘first-pass’ KKR-NLCPA calculation to demonstrate the differences in the resulting effective medium when using the KKR-NLCPA compared to the conventional KKR-CPA.

Given the comments above, the scattering path matrix $\hat{\underline{\tau}}^{ij}$ for a medium describing the average motion of an electron from site i to site j exactly is defined by

$$\hat{\underline{\tau}}^{ij} = \hat{\underline{t}}\,\delta_{ij} + \sum_{k\neq i} \hat{\underline{t}} \left(\underline{G}(\mathbf{R}_{ik}) + \widehat{\underline{\delta G}}(\mathbf{R}_{ik})\right) \hat{\underline{\tau}}^{kj} \tag{42}$$

Here a circumflex symbol denotes an effective medium quantity, an underscore denotes a matrix in angular momentum space, and the indices i, j run over all sites in the lattice. This equation can be seen as analagous to (3). Since (42) is translationally-invariant, the matrix elements $\hat{\underline{\tau}}^{ij}$ are also given by the BZ integral

$$\hat{\underline{\tau}}^{ij} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\mathbf{k} \left(\hat{\underline{m}} - \widehat{\underline{\delta G}}(\mathbf{k}) - \underline{G}(\mathbf{k})\right)^{-1} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \tag{43}$$

where $\hat{\underline{m}} = \widehat{\underline{t}^{-1}}$. By comparing (5) and (43), it is clear that the role of $\Sigma(\mathbf{k})$ is played by $-(\hat{\underline{m}} - \underline{\delta G}(\mathbf{k}))$. Following the derivation given in Section 2, the next step is to select an appropriate cluster and tile (see later in this section for more details), apply Born-von Karman boundary conditions to the cluster, and find the corresponding set of cluster sites $\{I\}$ and cluster momenta $\{\mathbf{K}_n\}$ satisfying (11). Then let us assume that we know the cluster quantities

$$\begin{aligned}
\left(\hat{\underline{m}}^I \delta_{IJ} - \widehat{\underline{\delta G}}(\mathbf{R}_{IJ})\right) &= \frac{1}{N_c} \sum_{\mathbf{K}_n} \left(\hat{\underline{m}} - \widehat{\underline{\delta G}}(\mathbf{K}_n)\right) e^{i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} \\
\left(\hat{\underline{m}} - \widehat{\underline{\delta G}}(\mathbf{K}_n)\right) &= \sum_{J} \left(\hat{\underline{m}}^I \delta_{IJ} - \widehat{\underline{\delta G}}(\mathbf{R}_{IJ})\right) e^{-i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)}
\end{aligned} \tag{44}$$

which are analagous to Σ_{cl}^{IJ} and $\Sigma_{cl}(\mathbf{K}_n)$. Now the cluster can be mapped to the lattice in reciprocal space in exactly the same way as Section 2 i.e. the scattering path matrix is represented by the set of coarse-grained values

$$\hat{\underline{\tau}}(\mathbf{K}_n) = \frac{N_c}{\Omega_{BZ}} \int_{\Omega_{\mathbf{K}_n}} d\mathbf{k} \left(\hat{\underline{m}} - \widehat{\underline{\delta G}}(\mathbf{K}_n) - \underline{G}(\mathbf{k})\right)^{-1} \tag{45}$$

and by using (11) the scattering path matrix at the cluster sites becomes

$$\hat{\underline{\tau}}^{IJ} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \left(\int_{\Omega_{\mathbf{K}_n}} d\mathbf{k} \left(\hat{\underline{m}} - \widehat{\underline{\delta G}}(\mathbf{K}_n) - \underline{G}(\mathbf{k})\right)^{-1} \right) e^{i\mathbf{K}_n(\mathbf{R}_I - \mathbf{R}_J)} \tag{46}$$

Again, physically this means that the ‘exact’ medium described by (42) has been replaced by an effective medium which is still translationally-invariant but the range of nonlocal correlations retained (described by $\widehat{\underline{\delta G}}(\mathbf{R}_{IJ})$) are restricted by the size of the cluster used to determine the medium. However, the above mapping was based on the assumption that we know the quantities in (44). To determine them, the impurity problem must be solved by generalising the conventional KKR-CPA argument in real space. This can be straightforwardly done by rearranging (42) for the effective medium in the form

$$\hat{\underline{\tau}}^{IJ} = \hat{\underline{t}}_{cl}^{IJ} + \sum_{K,L} \hat{\underline{t}}_{cl}^{IK}\, \hat{\underline{\Delta}}^{KL}\, \hat{\underline{\tau}}^{LJ} \tag{47}$$

where the effective cluster t-matrix is defined by

$$\hat{\underline{t}}_{cl}^{IJ} = \hat{\underline{t}}^{I} \delta_{IJ} + \sum_{K} \hat{\underline{t}}^{I} \left(\underline{G}(\mathbf{R}_{IK}) + \widehat{\underline{\delta G}}(\mathbf{R}_{IK})\right) \hat{\underline{t}}_{cl}^{KJ} \tag{48}$$

and describes all scattering within the cluster, whilst the cavity function $\underline{\underline{\widehat{\Delta}}}^{IJ}$ describes all scattering outside of the cluster. Since $\underline{\underline{\widehat{\Delta}}}^{IJ}$ describes the medium outside and is independent of the contents of the cluster, it may be used to define the impurity cluster path matrix

$$\underline{\tau}_{\gamma}^{IJ} = \underline{t}_{cl,\gamma}^{IJ} + \sum_{K,L} \underline{t}_{cl,\gamma}^{IK} \, \overline{\underline{\underline{\Delta}}}^{KL} \, \underline{\tau}_{\gamma}^{LJ} \tag{49}$$

where the impurity cluster t-matrix is defined by

$$\underline{t}_{cl,\gamma}^{IJ} = \underline{t}_{\gamma}^{I} \delta_{IJ} + \sum_{K} \underline{t}_{\gamma}^{I} \, \underline{G}(\mathbf{R}_{IK}) \, \underline{t}_{cl}^{KJ}. \tag{50}$$

for a fixed impurity cluster configuration γ. In other words, the effective cluster has simply been replaced by an ‘impurity’ cluster of real t-matrices with configuration γ and free-space structure constants ‘embedded’ in the (still undetermined) effective medium. The KKR-NLCPA self-consistency condition demands that there be no additional scattering from the cluster on the average i.e.

$$\sum_{\gamma} P_{\gamma} \, \underline{\tau}_{\gamma}^{IJ} = \underline{\widehat{\tau}}^{IJ}, \tag{51}$$

where P_{γ} is the probability of configuration γ occuring. The effective medium t-matrices and structure constant corrections are thus determined from a self-consistent solution of (46) and (51). After the medium has been determined, the site-diagonal part of the Green’s function (27) for any site I belonging to an impurity cluster of configuration γ embedded in the medium is given by

$$G_{\gamma}(E, \mathbf{r}_I, \mathbf{r}'_I) = \sum_{LL'} P_{\gamma} Z_L^{\gamma}(E, \mathbf{r}_I) \tau_{\gamma,LL'}^{II} Z_{L'}^{I}(E, \mathbf{r}'_I) - \sum_{L} P_{\gamma} Z_L^{\gamma}(E, \mathbf{r}_I) \tilde{J}_L^{\gamma}(E, \mathbf{r}'_I) \tag{52}$$

Therefore the partially-averaged cluster charge density measured at the site I, given that the cluster configuration is γ, is obtained from

$$\rho_{\gamma}(\mathbf{r}_I) = -\frac{1}{\pi} Im \int_{-\infty}^{E_F} G_{\gamma}(E, \mathbf{r}_I, \mathbf{r}_I) dE \tag{53}$$

The total average Green’s function and charge densities are obtained by summing over all γ, and any site in the cluster can be chosen to be site I since all cluster sites are equivalent after averaging over all γ.

KKR-NLCPA algorithm

For computational purposes it is not necessary to involve $\underline{\widehat{t}}_{cl}^{IJ}$ since this quantity includes the free-space structure constants which are not strictly needed (although they should be included in the formal multiple scattering derivation as above in order to facilitate the scattering within the cluster). Instead, it is easier to leave the free space structure constants inside the cavity i.e. renormalise $\underline{\underline{\widehat{\Delta}}} + \underline{\underline{G}} \rightarrow \underline{\underline{\widehat{\Delta}}}$ and simply work with the quantity $\underline{\underline{\widehat{m}}} - \underline{\underline{\widehat{\delta G}}}$. For clarity, it is convenient to label this quantity as $\underline{\underline{\widehat{X}}}$ so that $\underline{\widehat{X}}^{IJ} = \underline{\widehat{m}}\delta_{IJ} - \underline{\widehat{\delta G}}(\mathbf{R}_{IJ})(1 - \delta_{IJ})$. All real-space matrices in the algorithm are matrices in the cluster site and angular momentum index only (denoted by a double underscore) and all reciprocal-space matrices are diagonal i.e.

$$\underline{\underline{\widehat{X}}} = \begin{bmatrix} \underline{\widehat{X}}^{11} & \underline{\widehat{X}}^{12} & \underline{\widehat{X}}^{13} \cdots \\ \underline{\widehat{X}}^{21} & \underline{\widehat{X}}^{22} & \underline{\widehat{X}}^{23} \cdots \\ \underline{\widehat{X}}^{31} & \underline{\widehat{X}}^{32} & \underline{\widehat{X}}^{33} \ddots \end{bmatrix} = \begin{bmatrix} \underline{\widehat{m}} & \underline{\widehat{\delta G}}(\mathbf{R}_{12}) & \underline{\widehat{\delta G}}(\mathbf{R}_{13}) \cdots \\ \underline{\widehat{\delta G}}(\mathbf{R}_{21}) & \underline{\widehat{m}} & \underline{\widehat{\delta G}}(\mathbf{R}_{23}) \cdots \\ \underline{\widehat{\delta G}}(\mathbf{R}_{31}) & \underline{\widehat{\delta G}}(\mathbf{R}_{32}) & \underline{\widehat{m}} \ddots \end{bmatrix}$$

$$\underline{\underline{\widehat{X}}}(\mathbf{K}) = \begin{bmatrix} \underline{\widehat{X}}(\mathbf{K}_1) & 0 & 0\cdots \\ 0 & \underline{\widehat{X}}(\mathbf{K}_2) & 0\cdots \\ 0 & 0 & \underline{\widehat{X}}(\mathbf{K}_3) \\ & & & \ddots \end{bmatrix} = \begin{bmatrix} \underline{\widehat{m}} - \underline{\widehat{\delta G}}(\mathbf{K}_1) & 0 & 0\cdots \\ 0 & \underline{\widehat{m}} - \underline{\widehat{\delta G}}(\mathbf{K}_2) & 0\cdots \\ 0 & 0 & \underline{\widehat{m}} - \underline{\widehat{\delta G}}(\mathbf{K}_3) \\ & & & \ddots \end{bmatrix}$$

An example algorithm proceeds as follows:

1. For the first iteration make a guess for the effective matrix $\underline{\widehat{X}}^{IJ}$. For example place an average t-matrix (ATA) $\underline{\bar{t}} = P(A)\underline{t}^A + P(B)\underline{t}^B$ on each cluster site and set the off-diagonal terms $\underline{\widehat{\delta G}}(\mathbf{R}_{IJ})$ to zero.
2. Convert the matrix elements $\underline{\widehat{X}}^{IJ}$ to reciprocal space using (11).
3. Calculate the matrix elements $\underline{\widehat{\tau}}(\mathbf{K}_n)$ via $\underline{\widehat{\tau}}(\mathbf{K}_n) = \frac{N_c}{\Omega_{BZ}} \int_{\Omega_{\mathbf{K}_n}} d\mathbf{k} \left(\underline{\widehat{X}}(\mathbf{K}_n) - \underline{G}(\mathbf{k}) \right)^{-1}$ and convert to real space using (11).
4. Calculate the matrix elements $\underline{\widehat{\Delta}}^{IJ}$ by solving $\underline{\underline{\widehat{\Delta}}} = \underline{\underline{\widehat{X}}} - \underline{\underline{\widehat{\tau}}}^{-1}$.
5. Calculate $\underline{\tau}_{\gamma}^{IJ}$ for each impurity cluster configuration using $\underline{\underline{\tau}}_{\gamma} = \left(\underline{\underline{m}}_{\gamma} - \underline{\underline{\widehat{\Delta}}} \right)^{-1}$
6. Average $\underline{\tau}_{\gamma}^{IJ}$ over all 2^{N_c} configurations (with an appropriate probability distribution to include SRO if desired) to obtain a new effective path matrix at the cluster sites $\underline{\widehat{\tau}}^{IJ}$.
7. Calculate the new effective matrix elements $\underline{\widehat{X}}^{IJ}$ via $\underline{\underline{\widehat{X}}} = \underline{\underline{\widehat{\tau}}}^{-1} + \underline{\underline{\widehat{\Delta}}}$ using $\underline{\underline{\widehat{\Delta}}}$ from step 4 and $\underline{\underline{\widehat{\tau}}}$ from step 6. Note that the off-diagonal matrix elements of the new effective matrix $\underline{\underline{\widehat{X}}}$ will no longer be zero due to the configurational averaging in step 6.
8. Compare the new matrix elements $\underline{\widehat{X}}^{IJ}$ with those in step 1. If they are not equal to within the desired accuracy, repeat as necessary steps 2 → 8 using the new $\underline{\widehat{X}}^{IJ}$ until convergence within the desired accuracy is achieved.

Note that an efficient implementation of the KKR-NLCPA to the ferromagnetic alloy system $FePt$ has recently been given in [37]. In particular, [37] shows how convergence of the above algorithm can be stabilised by recasting into a form that goes back to the work of Mills [38], and details how computational effort can be reduced by making use of symmetry.

Choice of cluster

The restrictions on the choice of cluster in the NLCPA has been mentioned in Section 2. The construction for choosing suitable clusters and finding the cluster sites and cluster momenta satisfying (11) was first given in [15] in the context of the 2D square lattice, and generalised to realistic 3D lattices in [18–20]. Fig. 6 shows example small clusters and corresponding tiles for the commonly encountered bcc and fcc lattices. Significantly, since the simple cubic tiles here have the same cubic point-group symmetry as the underlying lattice, the reciprocal space integrations can be reduced to the usual $1/48^{th}$ irreducible wedge. Computationally, one can simply integrate over the irreducible parts of each tile, the total sum being the $1/48^{th}$ irreducible wedge of the original lattice. Note that KKR-NLCPA calculations have recently been carried out using $N_c = 8$ clusters in [39].

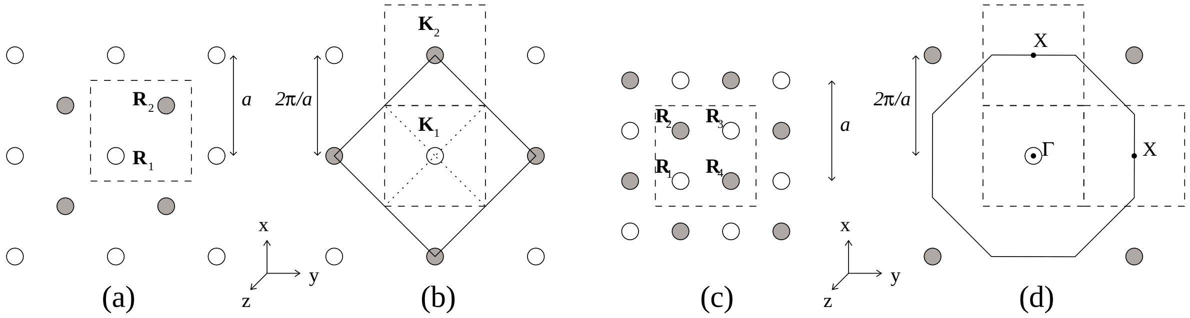


Figure 6: (a) Cross-section of a real-space tile (dashed line) for the bcc lattice with $N_c = 2$ cluster containing the points $\mathbf{R}_1 = (0, 0, 0)$ and $\mathbf{R}_2 = (a/2, a/2, a/2)$. The shaded sites lie out of the page. (b) Cross-section of the corresponding reciprocal-space tiles (dashed lines) for the $N_c = 2$ cluster, with $\mathbf{K}_1 = (0, 0, 0)$ and $\mathbf{K}_2 = (2\pi/a, 0, 0)$ at their centres. The shaded points lie out of the page and the solid line denotes a cross-section of the first BZ in the (k_x, k_y) plane. The BZ can be visualised as a cube with a pyramid attached to each of the six faces, and the dotted line shows a projection of such a pyramid into the k_z plane. (c) Cross-section of a real-space tile (dashed line) for a $N_c = 4$ cluster on the fcc lattice containing the points $\mathbf{R}_1 = (0, 0, 0)$, $\mathbf{R}_2 = (a/2, 0, a/2)$, $\mathbf{R}_3 = (a/2, a/2, 0)$ and $\mathbf{R}_4 = (0, a/2, a/2)$. The shaded sites lie out of the page. (d) Cross-section of the corresponding reciprocal-space tiles (dashed lines) for the $N_c = 4$ cluster, with $\mathbf{K}_1 = (0, 0, 0)$, $\mathbf{K}_2 = (2\pi/a, 0, 0)$, and $\mathbf{K}_3 = (0, 2\pi/a, 0)$ shown as the Γ point and the two X points. The fourth tile is centered at the X point $\mathbf{K}_4 = (0, 0, 2\pi/a)$ and is situated out of the page vertically above Γ. Again the shaded points lie out of the page and the solid line denotes a cross-section of the first BZ in the (k_x, k_y) plane.

Results

To illustrate the differences between the KKR-NLCPA and the conventional KKR-CPA as a result of nonlocal scattering correlations and chemical SRO, selected calculations are presented here for the $Cu_{50}Zn_{50}$ system using Cu and Zn potentials that come from self-consistent field SCF-KKR-CPA calculations. First, Fig. 7(a) shows DOS plots for pure Cu and pure Zn, and Fig. 7(b) shows a calculation for the long-range ordered $Cu_{50}Zn_{50}$ inter-metallic compound (which exists below the transition temperature). Since the energies of the Cu and Zn d-bands are very different, the system is said to be in the 'split band' regime. Physically, this means an electron travels more easily between like sites than between unlike sites and so this results in a narrowing of the Cu and Zn bands by a factor of two in the ordered calculation compared with the pure calculations [40]. Fig. 7(c) shows KKR-CPA results for disordered bcc $Cu_{50}Zn_{50}$. It is clear that the bands are widened and smoothened compared with the DOS for the ordered calculation. The component contributions from Cu and Zn impurity sites embedded in the KKR-CPA medium are also shown. Next, a KKR-NLCPA calculation for disordered $Cu_{50}Zn_{50}$ for a two-site cluster ($N_c = 2$) is shown in Fig. 7(d). First note that there is little observable difference in the total DOS compared with the KKR-CPA calculation. This is due to the small size of the cluster so that the difference due to the nonlocal scattering correlations shows up in detail only on a scale of ± 1 state/atom/Ry (see Ref. [20]). However the most striking aspect of the KKR-NLCPA calculation is that the component contributions to the total DOS from the four possible cluster configurations are apparent. The component plots here are the DOS measured at the first cluster site when a particular cluster configuration is embedded in the KKR-NLCPA medium, which is the Cu site for the Cu-Cu and

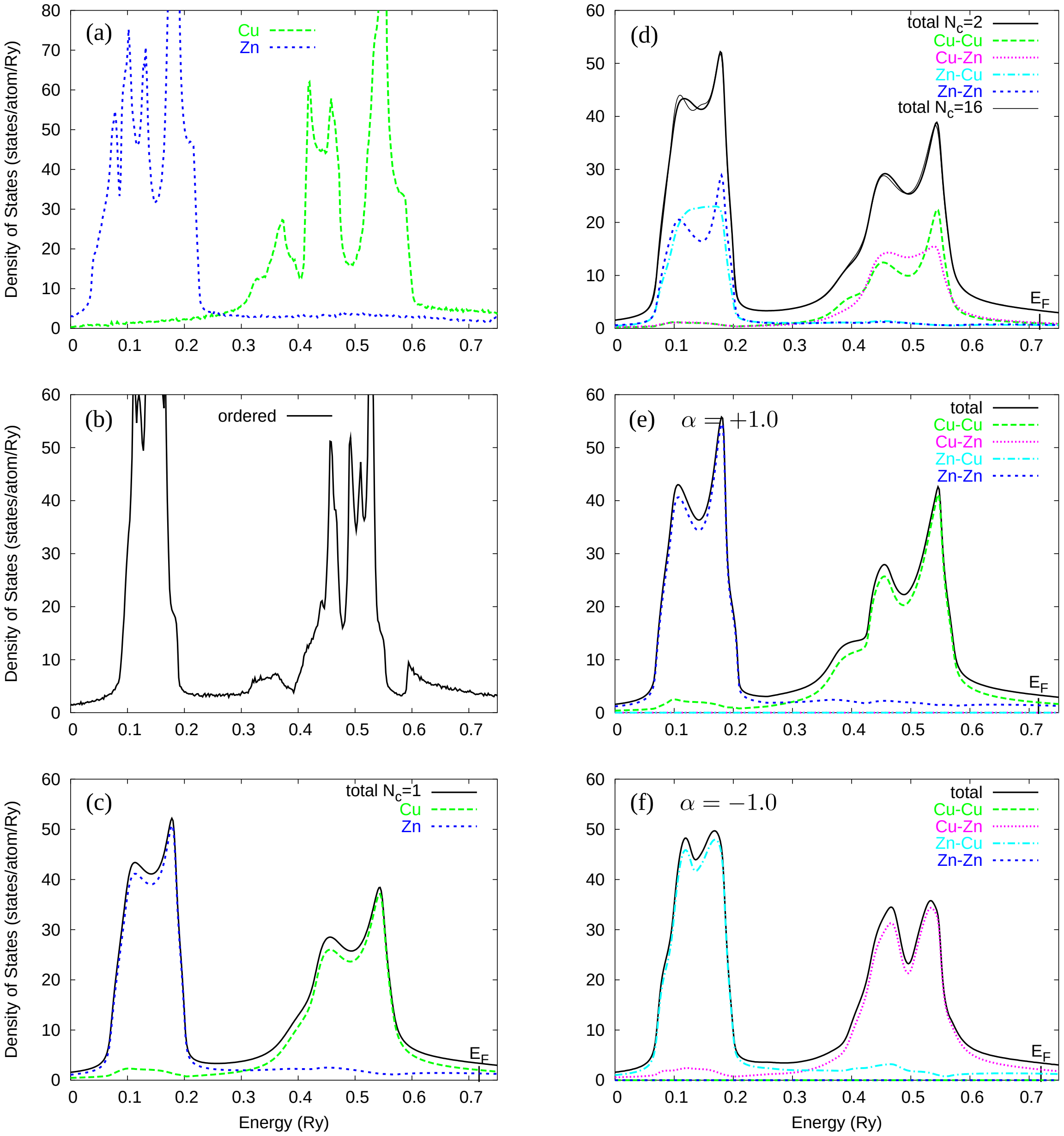


Figure 7: (a) Density of states (DOS) for pure Cu and pure Zn. (b) DOS for ordered $Cu_{50}Zn_{50}$. (c) Total average DOS for disordered *bcc* $Cu_{50}Zn_{50}$ using the KKR-CPA. Also shown are the contributions from the Cu and Zn components (single-site partially-averaged DOS). E_F is the Fermi energy. (d) Total average DOS for *bcc* $Cu_{50}Zn_{50}$ using the KKR-NLCPA with $N_c = 2$, along with the contributions from the 4 possible cluster configurations (cluster partially-averaged DOS) measured at the first site i.e. Cu for Cu-Cu, Cu-Zn, and Zn for Zn-Cu, Zn-Zn. (Owing to the translational invariance, contributions measured at the second site would give the same results with a simple reversal of the labels). Also shown are total DOS results for $N_c = 16$. (e) Same as (d) but with SRO parameter α=+1.0, corresponding to ideal short-range clustering. (f) Same as (d) but with SRO parameter α=-1.0, corresponding to ideal short-range ordering.

Cu-Zn configurations, and the Zn site for the Zn-Cu and Zn-Zn configurations. Crucially, owing to the translational invariance of the KKR-NLCPA medium, measurement at the second site gives the same results with a simple reversal of the labels of the Cu-Zn and Zn-Cu components. These component plots are particularly useful for interpreting the effects of SRO on the electronic structure. For a cluster of size $N_c = 2$, it is possible to include SRO between nearest neighbour sites only. This may be straightforwardly done by introducing the nearest neighbour Warren-Cowley SRO parameter α [41], and using probabilities defined as $P_{CuCu} = P^2_{Cu} + \alpha/4$, $P_{ZnZn} = P^2_{Zn} + \alpha/4$, $P_{CuZn} = P_{Cu}P_{Zn} - \alpha/4$, and $P_{ZnCu} = P_{Zn}P_{Cu} - \alpha/4$. For $Cu_{50}Zn_{50}$, $P_{Cu} = P_{Zn} = 0.5$ and so possible values in the range $-1 \leq \alpha \leq 1$, where -1, 0 and $+1$ correspond to ideal ordering, complete randomness, and ideal clustering. For example, at $\alpha = +1$ the probability of unlike pairs is zero and the total DOS is now completely dominated by the features of the Cu-Cu and Zn-Zn components, as shown in Fig. 7(e). As expected these features are reminiscent of the pure bands shown in Fig. 7(a). At the other extreme case $\alpha = -1$, as shown in Fig. 7(f), there are only contributions remaining from unlike pairs and the DOS in general has a closer resemblance to that of ordered $Cu_{50}Zn_{50}$ shown in Fig. 7(b).

4 Self-Consistent-Field (SCF)-KKR-NLCPA

The calculations presented in Section 3 were ‘first-pass’ KKR-NLCPA calculations only i.e. the potentials used were self-consistently determined using the conventional SCF-KKR-CPA, and then a single KKR-NLCPA calculation performed using these potentials. In other words, although the potentials were charge self-consistent with respect to the KKR-CPA medium, they were not charge self-consistent with respect to the new KKR-NLCPA medium. In order to appreciate the new physics that could be described by a charge self-consistent (SCF)-KKR-NLCPA [21], first recall that a disordered alloy as a whole is charge neutral. This implies that the effective medium representing the exact configurational average over all disorder configurations described by (42) shares this property. Moreover, since the medium is translationally-invariant, this implies that each site in the effective medium must be charge neutral. The problem with the conventional SCF-KKR-CPA method is that in setting up this medium, a single A or B impurity site embedded in the medium can only interact with this neutral environment i.e. the exchange of charge with other A and B sites belonging to specific disorder configurations is not taken into account. This in turn means there is an intersite Madelung electrostatic contribution missing in the SCF-KKR-CPA total energy expression for the alloy.

In order to see how to go beyond the SCF-KKR-CPA description of charges, it is important to realise that in a real alloy, say $Cu_{50}Zn_{50}$, we no longer only have one Cu and one Zn potential. This is because for any given disorder configuration, each Cu site and each Zn site will have a different environment i.e. differing numbers of Cu and Zn neighbours. This means that when charge redistributes itself to minimise the total energy for that configuration, there will in principle be a different potential on every site in the lattice [42]. In order to bridge the gap between the SCF-KKR-CPA and the exact result (within LDA), a charge self-consistent SCF-KKR-NLCPA must therefore go beyond a two-potential description of a binary alloy. The SCF-KKR-NLCPA achieves this by enforcing self-consistency with respect to a set of $N_c \times 2^{N_c}$ *cluster potentials* $\underline{v}_\gamma$ which depend on a set of partially-averaged *cluster charge densities* $\underline{\rho}_\gamma$. Due to the Born-von Karman boundary conditions imposed on the cluster, the charge self-consistent medium will be translationally-invariant and therefore each site will be charge neutral.

However, in setting up the medium, charge is allowed to transfer between the cluster sites and hence we will systematically gain an intersite Madelung electrostatic contribution to the total energy which was missing in the SCF-KKR-CPA.

In the interest of clarity it is useful to introduce the following notation. By measuring the partially-averaged (i.e. component) cluster charge density via (53) at each site in the cluster for the fixed configuration γ, we may define the cluster component charge density matrix $\underline{\rho}_{\gamma}(\mathbf{r})$ such that

$$\left[\underline{\rho}_{\gamma}(\mathbf{r})\right]_{II} = \rho_{\gamma}(\mathbf{r}_I)$$

where $\mathbf{r}_I$ implies that $\mathbf{r}$ restricted to lie within site I, and is measured from the nuclear position $\mathbf{R}_I$. Similarly, we introduce the cluster potential matrix $\underline{v}_{\gamma}(\mathbf{r})$ with site matrix elements

$$\left[\underline{v}_{\gamma}(\mathbf{r})\right]_{II} = v_{\gamma}(\mathbf{r}_I).$$

As an example, for the simple case of a two-site cluster for a binary alloy we will have $2^2 = 4$ cluster potential and cluster component charge density matrices, and will have $2^2 \times 2 = 8$ distinct single-site potentials (which can be reduced to 4 using symmetry e.g. $v_{AA}(\mathbf{r}_I) = v_{AA}(\mathbf{r}_J)$, $v_{AB}(\mathbf{r}_I) = v_{BA}(\mathbf{r}_J)$ etc.). For the configuration $\gamma = \{AB\}$ we have

$$\underline{v}_{\gamma}(\mathbf{r}) = \begin{bmatrix} v_{AB}(\mathbf{r}_I) & 0 \\ 0 & v_{AB}(\mathbf{r}_J) \end{bmatrix} \quad \text{and} \quad \underline{\rho}_{\gamma}(\mathbf{r}) = \begin{bmatrix} \rho_{AB}(\mathbf{r}_I) & 0 \\ 0 & \rho_{AB}(\mathbf{r}_J) \end{bmatrix}$$

Although the potentials are single-site quantities, it is still necessary to include the full configuration label. This is because although for example $v_{AB}(\mathbf{r}_J)$ is a 'B' site, $v_{AB}(\mathbf{r}_J)$ is not the same single-site potential as $v_{BB}(\mathbf{r}_J)$. The same notation must also be applied to the corresponding wavefunctions and cluster t-matrices when attempting to obtain self-consistent potentials e.g. for the configuration $\gamma = \{AB\}$ we have

$$\underline{\underline{Z}}_{\gamma} = \begin{bmatrix} \underline{Z}_{AB}(\mathbf{r}_I, E) & 0 \\ 0 & \underline{Z}_{AB}(\mathbf{r}_J, E) \end{bmatrix} \quad \text{and} \quad \underline{\underline{t}}_{cl,\gamma} = \begin{bmatrix} \underline{t}^{I}_{AB} & \underline{G}(\mathbf{R}_{IJ}) \\ \underline{G}(\mathbf{R}_{JI}) & \underline{t}^{J}_{AB} \end{bmatrix}$$

Total energy

By integrating Maxwell's relation $N = -\left(\partial\Omega/\partial\mu\right)$ for a fixed configuration where N is the number of electrons, it can be shown that the fundamental equation for the configurationally-averaged electronic grand potential is given by [10, 11]

$$\overline{\Omega} = \mu\overline{N}(\mu,\mu) - \int_{-\infty}^{\mu} dE\,\overline{N}(E,\mu) + \int_{-\infty}^{\mu} d\mu' \int_{-\infty}^{\mu'} dE\,\frac{\delta\overline{N}(E,\mu')}{\delta\mu'} \tag{54}$$

where $\overline{N}$ is the configurationally-averaged integrated density of states per site at constant temperature and volume, and μ is the electronic chemical potential. Adding the energy of the ion-ion interactions to $\overline{\Omega}$ gives the total internal energy of the system. The significance of the above equation is that only an approximation for $\overline{N}$ is required, together with its variation with respect to μ. Within the KKR-NLCPA, it can be straightforwardly shown that $\overline{N}$ is given by the Lloyd formula

$$\begin{aligned} \overline{N}(E,\mu) \quad = \quad & N_o(E) - \frac{1}{\pi}\frac{1}{\Omega_{BZ}} Im\left[\sum_{\mathbf{K}_n}\int_{\Omega_{\mathbf{K}_n}} d\mathbf{k}\;\; ln\|\widehat{\underline{t}}^{-1} - \widehat{\underline{\delta G}}(\mathbf{K}_n) - \underline{G}(\mathbf{k})\|\right] \\ - \quad & \frac{1}{\pi N_c} Im\left[\sum_{\gamma} P_{\gamma} ln\|\underline{\underline{\tau}}_{\gamma}^{-1}\| - ln\|\widehat{\underline{\underline{\tau}}}^{-1}\|\right] \end{aligned} \tag{55}$$

where N_o is the free-electron contribution and all other terms have been defined in Section 3. The determinants in the final term are over both the angular momentum and cluster-site indices. By evaluating $d\overline{N}/d\mu$, substituting into (54), and then performing the integration with respect to μ' by parts [21], an expression for the electronic grand potential in terms of the cluster potentials and cluster charge densities is obtained in the form

$$\begin{aligned} \overline{\Omega} &= \mu\overline{N}(\mu,\mu) - \int_{-\infty}^{\mu} dE\,\overline{N}(E,\mu) - \frac{1}{N_c}\sum_{\gamma} P_\gamma \sum_{I}\left(\int d\mathbf{r}_I \rho_\gamma(\mathbf{r}_I,\mu)\,v_\gamma(\mathbf{r}_I,\mu)\right) \\ &+ \frac{1}{N_c}\int_{-\infty}^{\mu} d\mu' \sum_{\gamma} P_\gamma \sum_{I}\left(\int d\mathbf{r}_I\, v_\gamma(\mathbf{r}_I,\mu')\frac{d\rho_\gamma(\mathbf{r}_I,\mu')}{d\mu'}\right) \end{aligned} \tag{56}$$

We now need a specific form for the cluster potential $\underline{v}_\gamma(\mathbf{r})$. As a generalisation of the SCF-KKR-CPA approach described in Section 3, we choose $\underline{v}_\gamma(\mathbf{r})$ to depend on the partially-averaged cluster charge densities $\underline{\rho}_\gamma(\mathbf{r})$ within the cluster and on the average charge density outside. So for a particular cluster configuration γ, we choose $\underline{v}_\gamma(\mathbf{r})$ within a cluster site I to take the form

$$\begin{aligned} v_\gamma(\mathbf{r}_I) &= \sum_{J}\int d\mathbf{r}'_J\,\frac{\rho_\gamma(\mathbf{r}'_J)}{|\mathbf{r}_I-\mathbf{r}'_J+\mathbf{R}_{IJ}|} - \sum_{J}\frac{Z^J_\gamma}{|\mathbf{r}_I+\mathbf{R}_{IJ}|} \\ &+ \sum_{n\notin C}\int d\mathbf{r}'_n\frac{\overline{\rho}(\mathbf{r}'_n)}{|\mathbf{r}_I-\mathbf{r}'_n+\mathbf{R}_{In}|} - \sum_{n\notin C}\frac{\overline{Z}^n}{|\mathbf{r}_I+\mathbf{R}_{In}|} + v^{xc}_\gamma\left[\rho_\gamma(\mathbf{r}_I)\right] \end{aligned} \tag{57}$$

where the sums in the first line are over all sites J (including $J = I$) belonging to the cluster, and the sums in the second line are over all sites n outside of the cluster. Notation has been introduced such that the nuclear charge on a cluster site I for the fixed cluster configuration γ is labeled as Z^I_γ. So the first and second terms in (57) represent the electronic and nuclear Coulomb contributions respectively at $\mathbf{r}_I$ from each site in the cluster for the fixed configuration γ. The average charge and nuclear densities placed on all sites outside the cluster are given by $\overline{\rho}(\mathbf{r}_n) = \sum_\gamma P_\gamma\rho_\gamma(\mathbf{r}_I)$ and $\overline{Z}^n = \sum_\gamma P_\gamma Z^I_\gamma$ respectively (note any cluster site I may be chosen to calculate these since all sites are equivalent after averaging over all cluster configurations, a consequence of the Born-von Karman boundary conditions imposed on the cluster). Since each site is neutral on the average (but *not independently from the other sites* as in the KKR-CPA), we have $\int d\mathbf{r}_n\,\overline{\rho}(\mathbf{r}_n) - \overline{Z}^n = 0$. However these contributions from outside the cluster should still be included as there is in general a multipole contribution arising from them (e.g. for a non-spherical charge distribution). The final term in (57) represents the exchange correlation potential [6, 7] at $\mathbf{r}_I$, given that the impurity cluster configuration is γ. Now inserting (57) into the final term of (56) and performing the integration with respect to μ' by parts [21] leads to the expression for the electronic grand potential in the form

$$\begin{aligned} \overline{\Omega} &= \mu\overline{N}(\mu,\mu) - \int_{-\infty}^{\mu} dE\,\overline{N}(E,\mu) - \frac{1}{N_c}\sum_{\gamma} P_\gamma \sum_{I}\int d\mathbf{r}_I\,\rho_\gamma(\mathbf{r}_I,\mu)\,v_\gamma(\mathbf{r}_I,\mu) \\ &+ \frac{1}{2}\frac{1}{N_c}\sum_{\gamma} P_\gamma \sum_{I}\sum_{J}\frac{\int d\mathbf{r}_I\,\rho_\gamma(\mathbf{r}_I)\left(\int d\mathbf{r}'_J\,\rho_\gamma(\mathbf{r}'_J) - 2Z^J_\gamma\right)}{|\mathbf{r}_I-\mathbf{r}'_J+\mathbf{R}_{IJ}|} \\ &+ \frac{1}{2}\frac{1}{N_c}\sum_{\gamma} P_\gamma \sum_{I}\sum_{n\notin C}\frac{\int d\mathbf{r}_I\,\rho_\gamma(\mathbf{r}_I)\left(\int d\mathbf{r}'_n\,\overline{\rho}(\mathbf{r}'_n) - 2\overline{Z}^n\right)}{|\mathbf{r}_I-\mathbf{r}'_n+\mathbf{R}_{In}|} \\ &+ \frac{1}{N_c}\sum_{\gamma} P_\gamma \sum_{I}\int d\mathbf{r}_I\,\rho_\gamma(\mathbf{r}_I)v^{xc}_\gamma\left[\rho_\gamma(\mathbf{r}_I)\right] \end{aligned} \tag{58}$$

In the above expression the first line represents the configurationally-averaged kinetic energy. The second line involves Coulomb interactions between all cluster sites for each fixed impurity configuration γ. This is because charge is allowed to transfer between the cluster sites and so there will be a net (and different) overall charge on each cluster site. After the average over all configurations γ is taken, charge neutrality per site will be restored, however we have gained the energy contribution given in the second line. The off-diagonal part of this term (i.e. when $J \neq I$) represents charge correlations between the cluster sites, such terms being absent in the conventional single-site KKR-CPA expression. An estimate of the Madelung contribution to the total energy per site missing in the single-site KKR-CPA may therefore be calculated by excluding the $J = I$ terms from the summation, yielding

$$E_{Madelung} = \frac{1}{2}\frac{1}{N_c}\sum_{\gamma} P_{\gamma} \sum_{I}\sum_{J \neq I} \frac{\int d\mathbf{r}_I\, \rho_{\gamma}(\mathbf{r}_I) \left(\int d\mathbf{r}'_J\, \rho_{\gamma}(\mathbf{r}'_J) - 2Z^J_{\gamma} \right)}{|\mathbf{r}_I - \mathbf{r}'_J + \mathbf{R}_{IJ}|} \tag{59}$$

for a cluster of size N_c. The third line of (58) represents the contributions from the average electronic and nuclear charges outside the cluster. The final term (fourth line) is the exchange-correlation energy. Finally, note that due to translational invariance, (58) and (59) may be simplified for computational purposes by removing the $1/N_c$ factor and the sum over cluster sites I, although the sum over J remains.

Charge self-consistency

Recall that in DFT for usual systems the total energy or Ω is stationary with respect to the ground-state charge density with the condition that the number of particles N is kept constant. The total energy within the conventional KKR-CPA maintains this variational property since Ω is stationary with respect to the partially-averaged charge densities $\rho_{\alpha}(\mathbf{r})$, where α is the atomic species i.e. $\delta\{\Omega - \mu\overline{N}\}/\delta\rho_{\alpha}(\mathbf{r}) = 0$ [11]. Significantly, as a generalisation of this it can be shown that the total energy expression within the KKR-NLCPA above is also variational i.e. $\delta\{\Omega - \mu\overline{N}\}/\delta(\rho_{\gamma}(\mathbf{r}_I)) = 0$ for each cluster configuration γ where $\mathbf{r}_I$ is a point within any cluster site I [21]. This variational property arises from the combined effects of the variational properties of DFT and the KKR-NLCPA, and establishes the charge self-consistency procedure which is briefly outlined below.

- Begin with an appropriate guess for the set of 2^{N_c} cluster potential matrices $\underline{v}_{\gamma}(\mathbf{r})$.
- Calculate the corresponding cluster t-matrices and use the KKR-NLCPA to determine the effective medium.
- Calculate the site-diagonal part of the partially-averaged cluster Green's functions $\underline{\underline{G}}_{\gamma}(\mathbf{r},\mathbf{r})$ and from these calculate the corresponding partially-averaged cluster charge densities $\underline{\rho}_{\gamma}(\mathbf{r})$.
- Using the charge densities above, reconstruct new cluster potentials $\underline{v}_{\gamma}(\mathbf{r})$. For a particular configuration γ, this is given by (57) for $\mathbf{r}$ lying within site I. This needs to be calculated for each I with $I = 1, .., N_c$ for the configuration γ.
- Compare with the previous cluster potentials and iterate to self-consistency.

Results

In order to explicitly demonstrate the differences between the new SCF-KKR-NLCPA calculations compared to the non-SCF KKR-NLCPA calculations given in Section 3, the same $bcc\ Cu_{50}Zn_{50}$ system is studied here. Fig. 8(b) shows a new SCF-KKR-NLCPA calculation for the DOS with $N_c = 2$ and no SRO (i.e. $\alpha = 0$ as defined in Section 3), together with the conventional SCF-KKR-CPA result. Again, the contributions from the four possible cluster configurations are also shown. It is clear that there is now an observable difference between the total DOS results using the new SCF-KKR-NLCPA compared to the SCF-KKR-CPA. This difference is plotted in Fig. 8(c), and integrates to zero since there are the same number of electrons (11.5) per site in both cases (the Fermi level has been subtracted separately for each total DOS plot in Fig. 8). As can be seen by comparing the corresponding component DOS plots with the non-SCF KKR-NLCPA results shown in Fig. 8(a), this difference arises from charge transfer between the cluster sites at certain energy regions. Here the energy regions in which this occurs are well separated since $Cu_{50}Zn_{50}$ is in the 'split band' regime.

Now let us consider the total energy of the system. Fig. 8(d) shows that there is an overall lowering of the total energy (of order 0.28 mRy) calculated using the SCF-KKR-NLCPA for $\alpha = 0$ compared with the SCF-KKR-CPA calculation. The Madelung contribution to the total energy calculated via (59) is -2.41 mRy. This compares favourably with values of -2.5 mRy and -2.67 mRy previously obtained using large supercell calculations in Refs. [43] and [44] respectively. Significantly, it is found that the difference in the total energy is much smaller than the magnitude of the Madelung contribution because changes in the potential contribution are largely compensated for by corresponding changes in the kinetic contribution when the Madelung term is included in such self-consistent calculations.

Finally let us consider the effects of SRO on the total energy of the system [45]. The physics of SRO plays a particularly important role near phase transitions where it is frequently a precursor for long range order and can be said to be driving the ordering process. In the ordering of the $Cu_{50}Zn_{50}$ solid solution into an intermetallic compound of $B2$ symmetry the system lowers its free energy by having unlike neighbours more frequently than like neighbours even in the disordered state, thereby lowering the temperature T_c where the system must finally order. We would therefore expect the total energy calculated using the SCF-KKR-NLCPA to be lower for negative values of α, corresponding to short-range ordering. Fig. 8(d) shows SCF-KKR-NLCPA calculations with $N_c = 2$ for the total energy plotted as a function of SRO (the corresponding DOS plots can be found in Ref. [21]). Reassuringly, it can be seen that the total energy is indeed lowered as α decreases. Furthermore the relationship between the total energy and SRO parameter is found in this case to be linear. However, it should be stressed that the SCF-KKR-NLCPA is a theory of the electronic structure for a given ensemble of alloy configurations and is not a theory for what configurations actually occur in practice. For example, the extreme case corresponding to $\alpha = -1.0$ (as defined in Section 3) means that only unlike pairs are included in the $N_c = 2$ cluster ensemble, a situation which would not occur in a real disordered alloy. The actual favoured amount of SRO at a given temperature above T_c would need to be found by minimising the corresponding free energy with respect to the SRO parameter α. This requires an expression for the configurational entropy term for the cluster with SRO, and would amount to a first-principles cluster variational method [46]. Work is currently being carried out on this development.

5 Conclusions and future work

A review of the nonlocal coherent-potential approximation (NLCPA) has been presented, both within the tight-binding framework and within first-principles multiple scattering theory (KKR-NLCPA). The

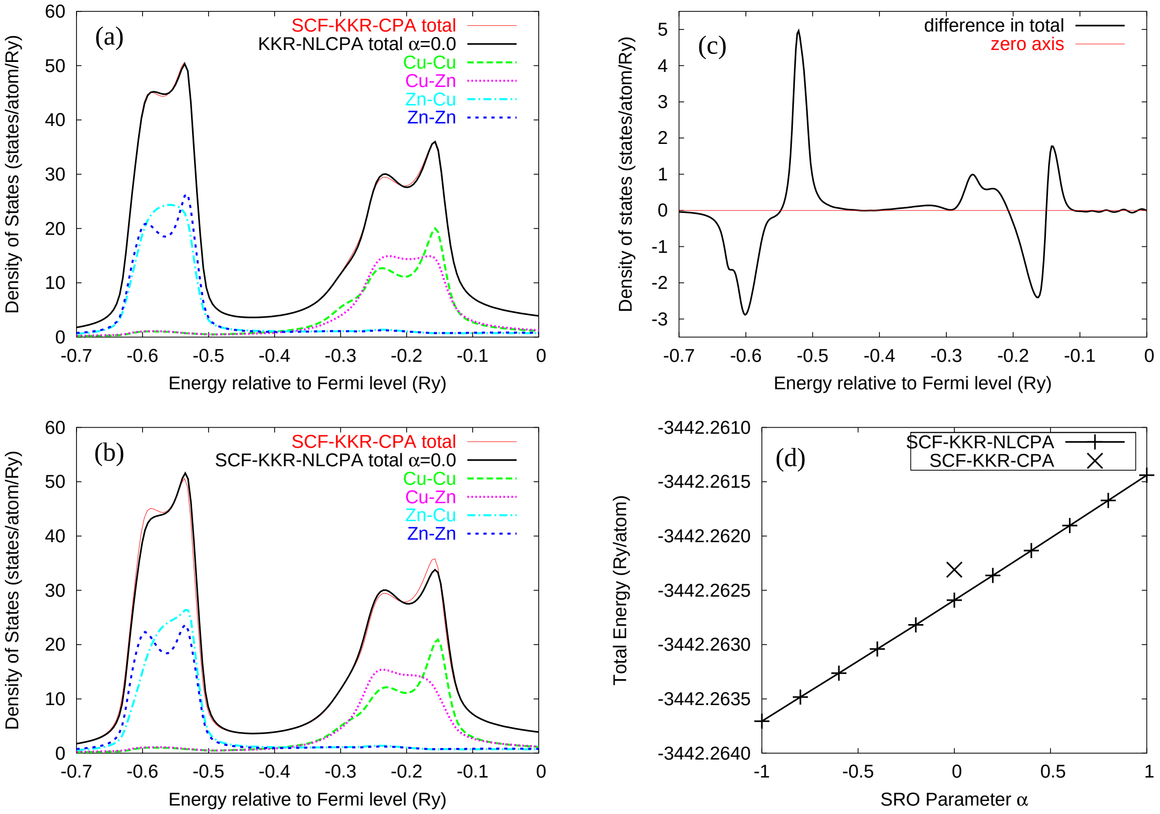


Figure 8: (Data obtained by A. Ernst) (a) Total average DOS for disordered bcc $Cu_{50}Zn_{50}$ using the (non-SCF) KKR-NLCPA with $N_c = 2$ and $\alpha = 0$. Also shown are the contributions from the four possible cluster configurations (measured at the first labelled site). The total conventional SCF-KKR-CPA result is also shown for comparison. (b) Same as above but using the new self-consistent-field (SCF)-KKR-NLCPA. Notice the differences in the cluster component contributions compared to (a) as a result of charge transfer. (c) Plot of the difference between the total SCF-KKR-CPA and total SCF-KKR-NLCPA results shown in (b) due to charge transfer. (d) Total energy for disordered bcc $Cu_{50}Zn_{50}$ using the SCF-KKR-NLCPA with $N_c = 2$ as a function of SRO parameter α. Also shown is the conventional SCF-KKR-CPA result (at $\alpha = 0$).

NLCPA generalises the conventional CPA approach to dealing with disordered systems by systematically enabling important short-range environmental effects present in the individual disorder configurations to be included in its configurationally-averaged description of the system. A fully charge self-consistent version of the theory (SCF-KKR-NLCPA) has been demonstrated by investigating the effects of charge-correlations and chemical short-range order on the $Cu_{50}Zn_{50}$ solid solution.

In regard to the computational issues of the method itself, the SCF-KKR-NLCPA has relatively low computational cost in comparison with supercell-based methods since the Brillouin zone integration does not scale as the cluster size increases. The only computational cost compared to the conventional SCF-KKR-CPA is due to averaging over the 2^{N_c} real-space cluster configurations, where N_c is the number of sites in the cluster. For calculations with small cluster sizes such as $N_c = 2$ and $N_c = 4$, there is therefore very little increase in computational cost over the conventional SCF-KKR-CPA method. Moreover, calculations with such cluster sizes are, for example, able to model the effects of nearest-neighbour SRO and are able to capture a large fraction of the Madelung energy in alloys. However, calculations for larger cluster sizes will be computationally very demanding and it will clearly be necessary to use importance sampling to greatly reduce the number of configurations. Furthermore, calculations for a simple 1D tight-binding model show that for cluster sizes below a critical value $N_{critical}$, results obtained using both periodic and anti-periodic Born-von Karman boundary conditions applied to the cluster should be combined. This can be straightforwardly carried out using the method proposed in Ref. [34], and has the advantage of yielding a spectral function with no discontinuities (thus facilitating its application to SRO studies of transport properties and Fermi surfaces). A systematic study of the convergence of the KKR-NLCPA with respect to cluster size is currently being carried out to establish the value of $N_{critical}$ for various realistic systems.

Finally, recall that the conventional SCF-KKR-CPA has been used as an electronic basis for a first-principles mean-field theory of the configurational statistical mechanics of the concentration fluctuations in alloys [47, 48]. In terms of future alloy-based work based on the SCF-KKR-NLCPA, it is clear that the cluster probabilities $\{P_\gamma\}$ used to calculate the total energy or electronic grand potential specify the corresponding cluster configurational entropy. These probabilities, which include a specification of SRO, may therefore be determined by constructing the appropriate free energy and minimizing it with respect to them (strain fluctuations [49] i.e. lattice displacements, could similarly be treated). This would amount to a fully first-principles cluster variational method [46] which can be expected to yield reliable alloy phase diagrams. Moreover, the SCF-KKR-CPA has also been adapted to treat valency fluctuations in pseudo-alloys [26], and adapted to deal with the disordered local moment (DLM) spin fluctuations in itinerant magnets at finite temperature [12, 13]. The SCF-KKR-NLCPA could similarly be adapted to investigate the creation of γ-like Ce atoms near the $\gamma - \alpha$ transition in a pseudo-alloy treatment of Ce, and to include correlations in the orientations of the local moments to facilitate the formation of the DLM state of Ni-rich systems.

Acknowledgments

Thanks to G. M. Batt, A. Ernst, B. L. Györffy and J. B. Staunton for collaborating on parts of the work reviewed in this highlight. This work was funded by EPSRC (U.K.).

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