Ψ_k Newsletter

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

Number 57   June 2003

1

Contents

1   Editorial

This newsletter we start with call for on-line proposals for plenary talks, topics and speakers of focused sessions, and topics and organizers of mini-colloquia for the 2004 Conference of the Condensed Matter Division of the European Physical Society. The following two sections **RTN1** and **RTN2** contain reports of recent meetings, including abstracts of presented papers. The final report on the activity of the TMR2 Network can be found in its dedicated section. It also contains scientific highlights of the involved partners. In the section of the **ESF Psi-k Programme** we have call for workshop proposals for 2004. There readers can also find useful information on funding participation of Americans in European workshops. In this newsletter there are a few announcements of meetings/workshops and they can be found in the dedicated sections of **RTN2**, **RTN3**, **ESF Psi-k**, as well as in the **General Workshop/Conference Announcements** section. The announcements of available positions can be found in the **RTN2** section, and in the **General Job Announcements** section. Abstracts of newly submitted papers or of papers published in less commonly read journals can be found in the usual **Abstracts** section. In this newsletter we also have a book announcement, just before the **Scientific Highlight of the Month** section. The scientific highlight is on **"An Introduction to Maximally-Localized Wannier Functions"** by Nicola Marzari (*MIT*), Ivo Souza (*Rutgers*) and David Vanderbilt (*Rutgers*). It contains 23 figures, mostly in colour. Please check table of contents for further details on the newsletter.

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 2003 workshops and hands-on courses (subject to funding). In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

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

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

2 General News

2.1 Call for Proposals for CMD-EPS 2004

Please see the announcement and call for proposals for the 20th Conference of the Condensed Matter Division of the European Physical Society in the **General Workshop/Conference Announcements** section. We encourage submissons of proposals on-line to

http://cmd.karlov.mff.cuni.cz/CMD/,

for plenary talks, topics and speakers for focused sessions, and topics and organizers for mini-colloquia. This is our opportunity to make a splash at this conference as the European Psi-k community. In particular, we should propose plenary invited speakers and symposia reflecting the interests of the electronic structure community.

3 News from the Research Training Network 1 (RTN1)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 Reports on RTN1 Workshops/Conferences

3.1.1 Report on Workshop on "Spin Mesoscopics"

EU RTN "Computational Magnetoelectronics"
NEDO "NanoMagnetoelectronics"
ESF Working Group "Magnetoelectronics"

Joint Workshop

on

"Spin Mesoscopics"

University of Twente,
Enschede,
March 15 - March 18, 2003

A workshop on "Spin Mesoscopics" was organized by Paul Kelly (Twente) and Gerrit Bauer (Delft) on the campus of the University of Twente over the weekend of March 15-183, 2003 and was attended by 63 participants. It was sponsored by the RTN "Computational Magnetoelectronics", the NEDO Network "NanoMagnetoelectronics", the ESF Working Group "Magnetoelectronics" and by the MESA+ Research Institute, University of Twente.

One of the principal aims of the workshop was to identify important basic physics issues which need to be resolved if spin-transport devices are to be reduced in size, and especially those where materials-specific computational techniques can play an important role. A topic discussed in considerable detail was current-induced magnetization reversal (CIMR), an alternative to the Lorentz switching of memory elements in magnetic random-access memory (MRAM) devices. We were fortunate to have some of the principal experimentalists working on CIMR attend the workshop: Buhrmann (Cornell), Sun (IBM, Yorktown) and Fert (Orsay) presented results of recent experiments on CIMR in very small structures. These talks were complemented with theoretical presentations by Zhang (Columbia, Missouri), Edward (Imperial College, London), Mathon (City U. London) and Stiles (NIST). The talk by Pratt (Michigan State) on measuring the angular magnetoresistance was closely related because the two effects involve transport between non-collinearly aligned magnets and a "spin-mixing" conductance is central to describing both. The same spin-mixing also formed an important element in the talks on spin-pumping by Brataas (Trondheim), on magnetization dynamics by Tserkovnyak (Harvard) and on enhanced Gilbert damping by Zwierzycki (Twente). The liveliness of the discussions during and after these talks was a good indicator of the interest and controversy raised by this subject.

Researchers very much want to realize spin-injection into semiconductors in order to add a spin degree of freedom. Molenkamp (Würzburg) reviewed his work using II-VI dilute magnetic semiconductors (DMS) as spin injectors while III-V DMSs were discussed by Ohno (Tohoku U. Sendai) and by Turek (Brno). Van Roy (IMEC, Leuven) discussed the difficulty of detecting the spin-polarization achieved on spin-injection into a semiconductor through tunnel junctions. Filip (Eindhoven) talked about the possibility of using a magnetic semiconductor or insulator as a spin filter. van Wees (Groningen) described his experiments of spin-injection and -detection through a tunnel barrier into one- and zero-dimensional non-magnetic metals and subsequent observation of the spin-precession. Jansen (Twente) and Parkin (IBM Almaden) introduced spin-dependent hot electron transport as the basic principle underlying the operation of hybrid devices such as the spin valve transistor (SVT) and the magnetic tunnel transistor (MTT). The difficulty of studying spin-transport through tunnel junctions in a realistic way was underlined by Wortmann (Jülich) who discussed the difficulties presented by the "simple" model system of Fe/MgO/Fe. A recent experimental observation of oscillations of the TMR when the thickness of a Cu "dusting" layer is varied was addressed theoretically using a tight-binding model and including disorder by Itoh (Nagoya). The state-of-the art in modelling disorder with first-principles methods was reviewed for a variety of systems by Xia (Beijing/Twente) while Ebert (München) illustrated for ferromagnet/semiconductor heterostructures the wide range of information which can be gained on such systems using a variety of band structure methods.

Ways of circumventing the problems bedevilling efficient spin-injection using half-metallic fer-

romagnets were discussed theoretically by Chioncel (Nijmegen) while Mavropoulos (Jülich) discussed theoretical calculations for a new class of zinc-blende compound which would be compatible with III-V semiconductors and are predicted to be half-metallic ferromagnets. Temmermann (Daresbury) reviewed the most important issues relating to half-metallic ferromagnetism of double perovskite structured materials.

The ultimate in miniaturization is achieved when devices have atomic dimensions. The state of the art of measuring electronic transport though a single molecule was presented by von Löhneysen (Karlsruhe) and calculations of spin-transport through atomic wires were discussed by Bagrets (Halle).

<div align="right">Paul Kelly</div>

List of Participants

Nr.	Name	e-mail
1.	Annett, James	james.annett@bristol.ac.uk
2.	Bagrets, Alexei	bagrets@physik.uni-halle.de
3.	Banerjee, Tamalika	T.Banerjee@el.utwente.nl
4.	Barnas, Jozef	barnas@main.amu.edu.pl
5.	Bauer, Gerrit	G.E.W.Bauer@TNW.TUDelft.nl
6.	Beckmann, Detlef	detlef.beckmann@int.fzk.de
7.	Bellini, Valerio	Bellini.Valerio@unimo.it
8.	Blügel, Stefan	s.bluegel@fz-juelich.de
9.	Brataas, Arne	Arne.Bartraas@phys.ntnu.no
10.	Brocks, Geert	G.H.L.A.Brocks@tnw.utwente.nl
11.	Buhrman, Robert	rab8@cornell.edu
12.	Chioncel, Liviu	chioncel@sa.kun.nl
13.	Costache, Marius	costache@phys.rug.nl
14.	Dederichs, Peter	P.H.Dederichs@fz-juelich.de
15.	Di Giustino, Leonardo	ldigiustino@unimo.it
16.	Di Lorenzo Antonio	A.DiLorenzo@TNW.TUDelft.nl
17.	Ebert, Hubert	Hubert.Ebert@cup.uni.muenchen.de
18.	Edwards, David	d.edwards@ic.ac.uk
19.	Fert, Albert	albert.fert@thalesgroup.com
20.	Filip, Andrei	a.t.filip@tue.nl
21.	Gerritsen, Sijmen	s.gerritsen@tnw.tudelft.nl
22.	Gokcan, Huseyin	H.Gokcan@el.utwente.nl
23.	Inomata, Koichiro	inomata@material.tohoku.ac.jp
24.	Inoue, Junichiro	inoue@nuap.nagoya-u.ac.jp
25.	Itoh, Hiroyoshi	itoh@nuap.nagoya-u.ac.jp
26.	Jansen, Ronnie	Ron.Jansen@el.utwente.nl
27.	Jaziri, Sihem	sihem.jaziri@esb.rnu.tn
28.	Kelly, Paul	P.J.Kelly@tnw.utwente.nl

29.	Khomyakov, Piotr	P.Khomyakov@tnw.utwente.nl
30.	Kovalev, Alexey	a.a.kovalev@tn.tudelft.nl
31.	Krawiec, Mariusz	m.a.krawiec@Bristol .ac.uk
32.	Kübler, Jürgen	kubler@fkp.tu-darmstadt.de
33.	Lerescu, Alex	a.i.lerescu@phys.rug.nl
34.	Levy, Peter	levy@nyu.edu
35.	Lezaic, Marjana	m.lezaic@fz-juelich.de
36.	Lodder, Cock	J.C.Lodder@el.utwente.nl
37.	Löhneysen van, Hilbert	H.vL@phys.uni.karlsruhe.de
38.	Manago, Takachi	t.manago@phys.rug.nl
39.	Martinek, Jan	martinek@ifmpan.poznan.pl
40.	Mathon, George	j.mathon@city.ac.uk
41.	Mavropoulos, Phivos	Ph.Mavropoulos@fz-juelich.de
42.	Molenkamp, Laurens	molenkmp@physik.uni-wuerzburg.de
43.	Novotny, Toms	TNO@MIC.DTU.DK
44.	Ohno, Yuzo	oono@riec.tohoku.ac.jp
45.	Parkin, Stuart	parkin@almaden.ibm.com
46.	Popescu, Voicu	vpopescu@lmd.de
47.	Postma, Ferry	F.M.Postma@el.utwente.nl
48.	Pratt Jr., William	pratt@pa.msu.edu
49.	Roy van, Willem	vanroy@imec.be
50.	Rudzinski, Wojciech	wojrudz@main.amu.edu.pl
51.	Rushchanskii, Konstantin	rushchanskii@mail.ru
52.	Stiles, Mark	mark.stiles@nist.gov
53.	Sun, Jonathan	jonsun@us.ibm.com
54.	Talanana, Mohand	M.Talanana@tnw.utwente.nl
55.	Temmerman, Walter	w.m.temmerman@dl.ac.uk
56.	Tserkovnyak, Yaroslav	yaroslav@physics.harvard.edu
57.	Turek, Ilja	turek@ipm.cz
58.	Ul-Haq Ehtsham	E.Haq@el.utwente.nl
59.	Vlaic, Petru	vlaic@ipcms
60.	Wees van, Bart	wees@phys.rug.nl
61.	Xia, Ke	kexia@aphy.iphy.ac.cn
62.	Zaffalon, Michele	zaffalon@phys.rug.nl
63.	Zwierzycki, Maciej	M.Zwierzycki@tnw.utwente.nl

Saturday, March 15th, 2003

08.30 – 09.00 **Registration**

08.50 – 09.00 **Opening**

Chair:	P.H. Dederichs

10.45 – 11.15 **Coffee**

Chair:	S.S.P. Parkin

12.45 – 14.15 **Lunch (Logica)**

Chair:	G.E.W. Bauer

16.15 – 16.45 **Coffee**

Chair:	J.C. Lodder
16.45 – 17.15	**D.M. Edwards**,
	Self-consistent theory of current-driven switching of magnetization

17.15 – 17.45	**J. Mathon**,
	Self-consistent theory of current-driven switching of magnetization

17.45 – 18.15	**Y. Tserkovnyak**,

18.15 – 18.45	**M. Zwierzycki**,

19.00 – 21.00	**Dinner (Logica)**
21.00 – 21.30	**Poster Preview**
21.30 –	**Posters/bar**

Sunday, March 16th, 2003

Chair:	J. Mathon
09.00 – 09.45	**M.D. Stiles**,

09.45 – 10.15	**A. Fert**,
	Magnetization reversal by injection and transfer of spin:

10.15 – 10.45	**B.J. van Wees**,
	Spin injection, spin transport and spin manipulation in mesososcopic

10.45 – 11.15	**Coffee**

Chair:	I. Inoue
11.15 – 11.45	**L.W. Molenkamp**,

11.45 – 12.15	**H. Ebert**,
	Electronic and magnetic and transport properties of

12.15 – 12.45	**J. Martinek**,

12.45 – 14.15	**Lunch (Logica)**

Chair:	**L.W. Molenkamp**

16.15 – 16.45	**Coffee**

Chair:	**H. Ebert**

19.00 – 21.00	**Dinner (Logica)**

21.00 –	**Posters/bar**

Monday, March 17th, 2003

Chair:	**A. Fert**

10.45 – 11.15	**Coffee**

Chair:	**W. van Roy**

12.15 – 13.15	**Lunch (Logica)**

13.15 – 19.00	**NEDO Excursion**

19.00 –	**NEDO Dinner**

Tuesday, March 18th, 2003

09.00 – 10.45	**NEDO meeting**

10.45 – 11.15	**Coffee**

11.15 – 12.45	**NEDO meeting**

12.45 – 14.15	**Lunch (Drienerburght)**

14.15 –	**Departure**

ABSTRACTS

MARCH 15, MORNING I

Angular variation of current-perpendicular-to-plane giant magnetoresistance in NiFe and CoFe exchange-biased spin valves

W.P. Pratt, Jr.,[1] L. Giacomoni,[2] B. Dieny,[2] R. Loloee[1] and M. Tsoi[1]

[1]Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA

[2]CEA/Grenoble, Département de Recherche Fondamentale sur la Matière Condensée, SP2M/NM, 38054 Grenoble Cedex 9, France

14

Abstract

We report measurements of the current-perpendicular-to-plane (CPP) giant magnetoresistance (MR) at 4.2 K for exchange-biased spin valves as a function of the angle (θ) between the magnetizations of the 'pinned' and 'free' ferromagnetic (F) layers. The following samples were studied: AF/Py/Cu(20nm)/Py,
AF/Py/Au(20nm)/Py and AF/CoFe/Cu(20nm)/CoFe, where Py = $Ni_{84}Fe_{16}$, CoFe = $Co_{91}Fe_9$, and AF = antiferromagnetic $Fe_{50}Mn_{50}$. The F-layer thicknesses were between 6 to 36 nm. We observe that the normalized CPP-MR, $R_{norm}(\theta)$, deviates significantly from a $[1 - cos^2(\theta/2)]$ behavior, where $R_{norm}(0) = 0$ and $R_{norm}(\pi) = 1$. Instead these data can be fit by a very simple equation of the form: $R_{norm}(\theta) = (1 - cos^2(\theta/2))/[1 + \chi cos^2(\theta/2)]$. The fitting parameter χ ranges between 0.7 and 1.3 for these samples. These results will be compared with recent theoretical work that also relate to high-current-density spin-transfer effects that induce magnetization switching in nanopillars. Work supported in part by US NSF grants DMR-98-09688 and 98-20135.

Spin pumping and magnetization dynamics

A. Brataas

Norwegian University of Science and Technology, N-7491 Norway

Abstract

Nanostructured ferromagnet-normal metal systems have recently attracted considerable attention. Slonczewski and Berger proposed that a spin-current could cause a switching of the magnetization orientation [1,2]. In their picture the spin-current induces a torque, a "spin-torque", on the spins of the conduction electrons, which subsequently transmit this torque to the magnetization. We demonstrate that there is also the reverse mechanism: Precessing ferromagnets inject a spin-current into adjacent conductors [3]. When the normal metal is a good sink this "pumping" of spins slows down the precession corresponding to an enhanced Gilbert damping in the Landau-Lifshitz equation. In the opposite regime, when the spin-flip relaxation time in the normal metal is long, "spin-pumping" opens the way to create a pure spin source ("spin battery") [4].

1. J. C. Slonczewski, J. Magn. Magn. Mater. **159**, L1 (1996).

2. L. Berger, Phys. Rev. B **54**, 9353 (1996).

3. Y. Tserkovnyak, A. Brataas, and G.E.W. Bauer, Phys. Rev. Lett. **88**, 117601 (2002).

4. A. Brataas, Y. Tserkovnyak, G.E.W. Bauer, and B. I. Halperin, Phys. Rev. B **66**, 060404 (R) (2002).

Spin transport with no free parameters

K.Xia[1], M. Zwierzycki[2], M. Talanana[2], P.J. Kelly[2], I. Turek[3] and G.E.W. Bauer[4]

[1] State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, China

[2]Faculty of Applied Physics and MESA$^+$ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

[3]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, CZ-616 62 Brno, Czech Republic

[4]Department of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Abstract

Interfaces play a crucial role in nanoscale electronic devices. The spin-dependence of the electronic scattering at an interface between a magnetic and a non-magnetic material is an essential element in understanding giant magnetoresistance in layered metallic structures and related effects such as junction magnetoresistance, point contact Andreev reflection at Ferromagnet/Superconductor contacts, enhanced Gilbert damping in layered magnetic materials, spin-injection into semiconductors, current-induced magnetization reversal etc. We have developed a method based on first-principles density functional theory and the tight-binding linear-muffin-tin orbital surface Green's function method to calculate spin-dependent scattering matrices for interfaces such as Co/Cu, Fe/Cr, Pb/Co and Fe/InAs. Disorder is treated by means of large lateral supercells. Without introducing any free parameters, quantitative agreement with experiment is obtained for a variety of the above phenomena. We review these applications and discuss how the calculations can be analysed in terms of simple models allowing us to make contact with phenomenological theories.

MARCH 15, MORNING II

Theory of quantum oscillation of tunneling magnetoresistance in junction with a nonmagnetic spacer

H. Itoh[1], J. Inoue[2,3], A. Umerski[4], and J. Mathon[5]

[1]Department of Quantum Engineering, Nagoya University, Nagoya 464-8603, Japan

[2]Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

[3]CREST, JST (Japan Science and Technology), Shibuya-ku, Tokyo 150-0002, Japan

[4]Department of Applied Mathematics, Open University, Milton Keynes MK7 6AA, U.K.

[5]Department of Mathematics, City University, London EC1V 0HB, U.K.

Abstract

Interfacial electronic structure of ferromagnetic tunneling junctions is an important ingredient for the tunnel magnetoresistance (TMR). Numerous experimental attempts have been made to show how TMR is affected by the spacer layer inserted at the interface of the junctions. Recently, a clear oscillation of TMR with respect to Cu layer thickness has been observed in high-quality $Co/Cu/Al_2O_3/NiFe$ junctions [1]. The characteristic features of the oscillation are i) TMR ratio oscillates around zero, ii) the period of the oscillations is determined solely by the Fermi wave vector k_F or the spanning wave vector of Cu Fermi surface belly, and iii) the amplitude of the oscillation decays with increasing Cu thickness.

Although there are several theoretical works on the oscillatory TMR, the reasons for vanishing of the average TMR and selection of the gamma-point TMR oscillation period are not clarified yet. In this work, we will make a theoretical explanation for the characteristic features of the observed oscillation in TMR by treating both the coherence of the electron propagation and the effect of disorder properly.

We consider a FM/I/NM/FM junction and adopt a single orbital tight-binding model, where FM, I, and NM are ferromagnetic lead, insulating barrier, and nonmagnetic spacer, respectively. By considering the electronic structure of Co and Cu, we choose parameters so that quantum well is formed at NM for minority spin states. We treat disorder in amorphous Al_2O_3 simply as on-site potential randomness. Conductance is calculated using the Kubo formula and CPA with vertex corrections.

It is shown that i) the disorder decreases the average value of the TMR ratio to zero, ii) increasing barrier thickness and the disorder increase the amplitude of the k_F oscillation period relative to the cut-off k-point k_{cp} period in TMR, and iii) the amplitude of the oscillation is inversely proportional to the spacer thickness. We conclude that momentum selection due to the insulating barrier and opening up new conduction channel via quantum well states due to the disorder are crucial to explain all the essential features of experimental results. We further show that the calculated results can be reproduced by the stationary phase approximation, which implies that this technique is applicable to a realistic multi-orbital model of the tunneling junction.

[1] S. Yuasa, T. Nagahama, and Y. Suzuki, Science **297** (2002) 234.

Spin injection and virtual magnon excitations: role of impurity and interface states

L. Chioncel,[1] R.A. de Groot,[1] M.I. Katsnelson,[2] G.A. de Wijs[1] and A.I. Lichtenstein[1]

[1]University of Nijmegen, 6500 GL, The Netherlands
[2]Uppsala University, S-751 21 Uppsala, Sweden

Abstract

We discuss factors that influence the 100% spin polarization in spin injection devices at finite temperatures. The effects of different interface and impurity states can be studied and optimized using LDA supercell calculations. We carried out such calculations on the prototype half-metallic ferromagnet NiMnSb. At finite temperatures an important effect on electronic structure comes from virtual magnon excitations. In the framework of Dynamical Mean Field Theory (DMFT) these excitations give rise to the existence of non-quasiparticle states above the Fermi level in the minority spin channel. We analyze the interaction of a sharp one-electron resonance due to a non-magnetic impurity (or interface) state with the non-quasiparticle states. Important consequences on electronic structure, magnetism and conduction electron spin polarization are discussed.

Diluted magnetic semiconductor double quantum dot: Zeeman splitting and magnetization

A. Hichri, S. Jaziri*

*Dpartement de Physique, Facult des Sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisie

Laboratoire de Physique de la Matire Condense, Facult des Sciences de Tunis, Tunisie

Abstract

We present a theoretical study of the valence and conduction band states in diluted magnetic semiconductor (DMS) $Cd_{0.57}Mn_{0.43}$ Te double quantum dot (DQD) structure. As a consequence of confinement in three directions, the hole states in a DQD are known to be mixtures of heavy and light hole components. Due to a strong p-d exchange interaction in DMS, the relative contribution of this components is strongly affected by an external magnetic field, a feature that is absent in non magnetic DQD. Thus the giant spin splitting (GSS) of excitonic states in DMSs is mainly determined by the spin splitting of the hole states. Since we note a crossing between the lowest states, which can be observed as a pronounced jump in the magnetization of a perpendicular magnetic field of a few T. We determine the exchange splitting as a function of magnetic field and the inter dot distance within the Heitler-London approximation of molecular physics and by including the Coulomb interaction. This result is refined by using the Hund-Mulliken molecular-orbit approach.

Figure 1. Magnetic field dependence of the magnetization.
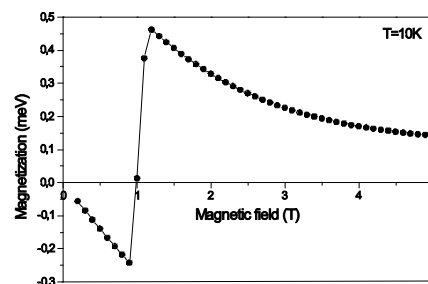
March 15, Afternoon I

Spin transfer and spin transport in magnetic nanostructures

Robert Buhrman

Cornell University

Abstract

I will discuss recent results obtained at Cornell from studies using magnetic F-N-F nanopillars of the magnetic switching and magnetic excitation of thin film nanomagnets by spin-polarized currents. We have made extensive measurements of the dependence of the

critical current for magnetic switching on the nanopillar parameters and have examined the differing roles of applied fields and polarized currents on altering the effective energy barrier for magnetic reversal. The experimental results all appear to be in accord with the basic spin torque model of Slonczewski with this spin transfer occurring predominately at the N-F interface due to the spin-dependent reflectivity of the interface. I will also discuss some very recent results where the high frequency dynamics of the spin-torque excited nanomagnet have been examined directly by measurement of its microwave emission under dc current basis. In general the results here are also in accord with the Slonczewski spin torque model although in the strongly driven regime chaotic behavior is observed that is not predicted in this model. Finally if time permits I will speak briefly about some spin dependent ballistic hot electron transport experiments and the effect of interfaces on this transport.

Transverse spin currents in the 3d transition-metal ferromagnets

Jianwei Zhang, Peter M Levy[1], Shufeng Zhang[2] , and Vladimir P. Antropov[3]

[1]Physics, New York University, New York, NY 10003, USA
[2]Physics, University of Missouri, Columbia, MO,6521, USA
[3]Ames Laboratory, Iowa State University, Ames Iowa 50011, USA

Abstract

When a spin polarized current enters a 3d transition-metal ferromagnet the component transverse to the magnetization is absorbed both at the interface and within some distance inside the ferromagnet. This is the mechanism by which spin angular momentum is transferred from a current to the background magnetization and thereby induces switching of a free magnetic layer. Based on ab-inito calculations of the band structure of these ferromagnets the length scale within which the transverse component is absorbed is generally less than 1 nm [1]. To explore how spin accumulation might alter this distance we have solved the Boltzmann equation for current across two noncollinear magnetic layers; this is an extension of the problem solved by Valet and Fert where the layers were either parallel or antiparallel.

The Boltzmann equation for spin transport involves the four components of a spinor; it is usually reduced to separate equations for the charge and spin currents by making suitable approximations so that one is left with a spin diffusion equation. The validity of these approximations when the magnetic layers are not collinear is precisely what we want to test; therefore we have solved the Boltzmann equation in the two layers without making the conventional approximations. Our solution gives us the length scale over which there exists a component of the spin current transverse to the local magnetization. As our solution of the spin current contains contributions from spin accumulation, our length scale differs from that found only from the band structure.

The essential parameter controlling the transverse length scale is the exchange coupling between electrons at the Fermi level, and the rest of the Fermi sea. We have calculated the energy resolved exchange coupling parameter between electrons in different orbitals on the Fermi surface of Fe, Co and Ni, by doing ab-initio calculations that maintains the transverse as well as the longitudinal degrees of freedom of spin. We find that on average this "s-d" exchange coupling can be up to one order of magnitude smaller than the Stoner

band splitting, which is the parameter that is conventionally used to estimate this coupling. We will discuss the implications of this for the current driven transverse spin accumulation in magnetically multilayered structures. *Work supported in part by the National Science Foundation and the Department of Energy.*

[1] M.D. Stiles and A. Zangwill, Phys. Rev. B **66**, 014407 (2002).

Spin-torque transfer in spin-valve magnetic nanojunctions

J.Z. Sun, M.J. Rooks, and R.H. Koch

IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, NY 10598

Abstract

A two terminal spin-injection device is fabricated using a nano-stencil process with a Co-Cu-Co stack. The stack can be deposited both by sputtering and by electron beam evaporation. A better edge definition is observed in evaporation-deposited films under cross-section transmission electron microscopy. Both methods succeeded in producing junctions with sub-100nm lateral dimensions and show spin-transfer-induced magnetic switching. Transport measurements reveal possible competition between coherent magnetic rotation and spin-wave generation, both may originate from spin-transfer excitation. A model based on a modified Landau-Lifshitz-Gilbert equation is developed to describe the quantitative behavior of the device.

MARCH 15, AFTERNOON II

Self-consistent theory of current-driven switching of magnetization
I: Basic formulation

D.M. Edwards[1], J. Mathon[2], F. Federici[1,2], and A. Umerski[3]

[1]Department of Mathematics, Imperial College, London SW7 2AZ, UK
[2]Department of Mathematics, City University, London EC1V OHB, UK
[3]Department of Applied Mathematics, Open University, Milton Keynes, MK7 6AA, UK

Abstract

In most experiments on current-driven switching of magnetization the current is varied slowly so that the system may be considered as passing through a sequence of steady states.

Such non-equilibrium steady states are conveniently studied using the Keldysh formalism in which simple steady state conditions are automatically satisfied. These conditions state that the torque on a magnetized atomic plane due to net inflow of spin current is exactly cancelled by the torque due to a local anisotropy field. An essential feature of the theory is a self-consistent treatment of the switching ferromagnet so that the magnetization is always in the direction of the local exchange field. The present method differs from that of Slonczewski in that the anisotropy field is included from the outset in the microscopic calculation and to study the steady state no Landau-Lifshitz equation is needed. An important difference from Slonczewski's approach is that the spin-transfer torque vector is not confined to the plane containing the magnetizations of the polarizing and switching ferromagnets. The consequences of our new approach have been explored and the first results are reported in the next talk.

Self-consistent theory of current-driven switching of magnetization
II: Results

J. Mathon[1], D.M. Edwards[2], F. Federici[1,2], and A. Umerski[3]

[1]Department of Mathematics, City University, London EC1V OHB, UK

[2]Department of Mathematics, Imperial College, London SW7 2AZ, UK

[3]Department of Applied Mathematics, Open University, Milton Keynes, MK7 6AA, UK

Abstract

General Keldysh formalism described in Part I shows that the component of the spin-transfer torque vector lying in the plane containing the magnetizations of the polarizing and switching magnets (Slonczewski torque) is always accompanied by an out-of-plane component. The in-plane (Slonczewski) component, referred to a system of coordinates with z-axis parallel to the spin quantization axis of the switching magnet, is denoted by $T_\parallel^{sc}$. The out-of-plane component is denoted by $T_\perp^{sc}$. The Keldysh formalism further shows that the out-of-plane $T_\perp^{sc}$ is proportional to the in-plane component $S_\parallel^{acc}$ of the spin accummulated in the switching magnet. Similarly, $T_\parallel^{sc} \propto S_\perp^{acc}$, the proportionality factor being in both cases the exchange splitting of the majority and minority bands of the switching magnet. The existence and physical origin of the out-of-plane spin-current torque is thus explained. However, the relative magnitude of the components $T_\perp^{sc}$ and $T_\parallel^{sc}$ is system dpendent. The results of microscopic calculations of $T_\perp^{sc}$ and $T_\parallel^{sc}$, using a single-orbital tight-binding model, are presented. They show that, depending on the parameters of the polarizing and switching magnets and of the non-magnetic spacer, all three cases $T_\perp^{sc} >> T_\parallel^{sc}$; $T_\perp^{sc} << T_\parallel^{sc}$; and $T_\perp^{sc} \approx T_\parallel^{sc}$ can occur. Since the spin-transfer torque is equal to the spin current absorbed by the switching magnet, calculations of the spin current before and after the switching magnet are essential. These show that, in some cases, only a fraction of the spin current incident on the switching magnet is converted into torque. Conversely, zero incident spin current can result in a non-zero torque on the switching magnet. In the case when the magnetizations of the polarizing and switching magnets are initially parallel (antiparallel), the existence of an out-of-plane torque means that current-induced switching can occur as

a sequence of steady states described in Part I. The switching path of such steady states, in which the spin-current torque balances the local anisotropy torque, is determined explicitly from a microscopic calculation. The critical switching currents are estimated for the single-orbital tight-binding model and preliminary results for a fully realistic Co/Cu/Co system are also presented. Finally, it is discussed how switching via a sequence of steady states and dynamical Slonczewski-type switching could be distinguished experimantally.

Dynamic stiffness of spin valves

Yaroslav Tserkovnyak[1], Arne Brataas[2], Gerrit E. W. Bauer[3]

[1]Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA

[2]Department of Physics, Norwegian University of Science and Technology,
N-7491 Trondheim, Norway

[3]Department of NanoScience, Delft University of Technology,
2628 CJ Delft, The Netherlands

Abstract

The dynamics of the magnetic order parameters of ferromagnet/normal-metal/ferromagnet spin valves and isolated ferromagnets may be very different. We investigate the role of the nonequilibrium spin-current exchange between the ferromagnets in the magnetization precession and switching. We find a (low-temperature) critical current bias for a coherent current-induced magnetization excitation in spin valves, which unifies and generalizes previous ideas of Slonczewski and Berger. In the absence of an applied bias, the effect of the spin transfer can be expressed as magnetic-configuration dependent Gilbert damping.

Gilbert damping enhancement from first principles

M. Zwierzycki[1], P.J. Kelly[1], K. Xia[2], Yaroslav Tserkovnyak[3], Arne Brataas[4],
G.E.W. Bauer[5]

[1]Faculty of Applied Physics and MESA$^+$ Research Institute, University of Twente, P.O.
Box 217, 7500 AE Enschede, The Netherlands

[2]State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy
of Sciences, P.O.Box 603, Beijing 100080, China

[3]Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA

[4]Department of Physics, Norwegian University of Science and Technology,
N-7491 Trondheim, Norway

[5]Department of Applied Physics and DIMES, Delft University of Technology,
Lorentzweg 1, 2628 CJ Delft, The Netherlands

Abstract

Precession of the magnetization in a ferromagnet results in the transfer of spins into adjacent normal metal layers. This "spin pumping" leads to the enhancement of the Gilbert

damping which can be observed in FMR experiments. The enhancement of the damping parameter can be expressed in terms of the elements of the scattering matrix of the embedded ferromagnetic layer. Here we report the first principles calculations of Gilbert damping for a number of systems of current interest using the TB-LMTO surface Green's function method. The efficiency of the method allows us to treat the disordered layers using large lateral superlattices. We consider two limiting cases - the very thick layers where the damping is determined by the reflecting properties of the interface ("mixing conductance") and the case of ultrathin layers when it is necessary to evaluate also the transmission through the ferromagnetic layer. In the latter case we study the thickness dependence of dumping.

MARCH 16, MORNING I

Anatomy of spin-transfer torques

M.D. Stiles,[1] and A. Zangwill[2]

[1]National Institute of Standards and Technology, Gaithersburg, MD 20899-8412, USA
[2]Georgia Institute of Technology, Atlanta, GA, 30332, USA

Abstract

A current passing through two ferromagnets separated by a non-magnetic spacer layer exerts a torque on each magnetization whenever the two magnetization directions are not parallel. We have modeled this behavior with a hierarchy of calculations. To start, we have computed the spin-dependent reflection and transmission amplitudes from first-principles quantum mechanical calculations. These amplitudes determine the fate of electrons that scatter from a interface with a ferromagnet. The calculations show that the transverse component of the incident spin current is essentially absorbed close to the interface. The absorbed spin current corresponds to a torque on the electrons by the ferromagnet with a corresponding reaction torque exerted on the magnetization close to the interface. Using these results as boundary conditions, we have derived and solved (numerically) a matrix Boltzmann equation to determine the transport in a Co/Cu/Co multilayer. In these calculations, spin-flip scattering (in the leads or in the magnets) plays an important role by polarizing the current in response to the spin-dependent resistances in the magnets. From the spin current and the boundary conditions, we compute the torques on the magnetizations.

Magnetization reversal by injection and transfer of spin: Experiments and theory

A. Fert[1], V. Cros[1], J.M. George[1], J. Grollier[1], H. Jaffrés[1], A. Hamzic[2], G. Faini[3], J. Ben Youssef[4], H. Le Gall[4]

[1]Unité Mixte de Physique CNRS-Thomson CSF, 91404 Orsay, France,

[2]Faculty of Sciences, University of Zagreb, Croatia,
[3]L2M-CNRS, 92250 Bagneux, France
[4]Laboratoire de Magnétisme de Bretagne, 29285 Brest, France.

Abstract

Slonczewski (and also Berger) predicted in 1995 that the magnetization of a magnetic layer can be reversed by spin transfer from a spin-polarized current injected into the layer. Convincing experiments have been now achieved and several theoretical approaches, extending the initial theory, have been recently developed for the interpretation of the existing experimental data. The first part of the talk is the presentation of experiments performed on Co/Cu/Co submicronic pillars fabricated by an e-beam lithography method. In a first type of experiment, we measure the critical current needed to switch the magnetic configuration of the trilayer from parallel to antiparallel (or antiparallel to parallel) and we study its dependence on the layer thickness, applied field and temperature. In another type of experiment, we use the current-induced interaction to control the magnetic configuration of the trilayer (parallel or antiparallel) and thus enhance or suppress the GMR. In the second part of the talk, I present the theoretical model we have developed for the interpretation of the experiments. This model is based on a self-consistent calculation of the longitudinal and transverse components of the spin current throughout the multilayered structure in the limit of quasi-interfacial spin transfer. The torques acting on the magnetic layers are derived from the transverse component of the spin current injected into each layer. I will compare our results for the torque with what is expected in other models and other limits. The critical currents are then calculated by introducing the torque in a LLG equation and I will discuss the different behaviors expected in different ranges of applied field (direct reversal or maintained precession). The experimental results are finally compared to the theory, with special focus on the interpretation of the critical current densities and the discussion of the effects of an applied field.

Spin injection, spin transport and spin manipulation in mesososcopic 1-D and 0-D metal systems

B.J. van Wees

Department of Applied Physics and Materials Science Centre, Groningen University

Abstract

I will give an overview of recent experiments where we employ ferromagnetic tunneljunctions to inject a spin polarized current into a non-magnetic metal and detect the resulting spin accumulation. We have studied spin transport in 1-dimensional systems, where we have observed controlled spin precession by an applied magnetic field [1]. Recently we succeeded to fabricate and study spin injection into a submicron aluminium island, where all 3 dimensions were shorter than the spin relaxation length [2].
[1] F.J. Jedema et al., Nature 416, 715 (2003)
[2] M. Zaffalon et al., in preparation

Spin injection and detection in semiconductors

L.W. Molenkamp

Physikalisches Institut der Universität Würzburg, Am Hubland, 97074 Würzburg,
Germany

Abstract

II-VI Dilute Magnetic Semiconductors have proven to be very useful in building an all-semiconductor platform for spintronics - so far they provide the only viable route to establish robust spin-polarized current injection into a non-magnetic semiconductor in the diffusive transport regime. The reasons for this become apparent from a simple two-current model, which predicts that spin-injection into a semiconductor can, within linear response, only readily be achieved from a ferromagnetic injector that has (i) a resistivity that is comparable to the semiconductor and (ii) preferably is 100% spin-polarized. Both of these criteria can be met in magnetic semiconductors, but (so far) are hard to achieve using other materials. Experimentally, we demonstrate how the injection of a spin-polarized current leads to a novel type of magnetoresistance (which we dubbed Large Magneto Resistance), reaching magnetoresistance changes of up to 30%. While these experiments were performed in the regime of linear (spin-) transport, we soon found that spin injection into semiconductors may be subject to strong non-linearities at somewhat elevated bias. We present experiments and modeling that demonstrate that a main mechanism leading to these non-linearities is a band-bending at the magnet-non-magnet interface. A second mechanism leading to non-linearities is the occurrence of drift effects in low-doped semiconducting material. We present an analysis of the device physics of the II-VI Spin-Light Emitting Diode (Spin-LED), a device that demonstrates a strongly (up to 90%) spin-polarized current at high bias, that demonstrates that field-effects are responsible for the efficient spin injection in these structures. Finally, I will discuss some aspects of our recent work on II-VI resonant tunneling diodes (RTDs), containing a II-VI DMS as well material. These RTDs exhibit a very pronounced splitting of the resonance peak at finite magnetic field, which can be ascribed to the giant Zeeman splitting in the well. Such devices could be put to use as voltage-controlled spin-selective injectors and detectors.

Electronic and magnetic and transport properties of ferromagnet-semiconductor heterostructure systems

H. Ebert,[1] M. Košuth,[1] V. Popescu,[1] A. Perlov,[1] J. Minár,[1]
R. Zeller,[2] N. Papanikolaou,[3] and P. H. Dederichs[2]

[1] Department Chemie/Physikalische Chemie, University of Munich, Butenandtstr. 5-13,
81377 Munich, Germany
[2] Inst. für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913,

D-52425 Jülich, Germany

3 Institute of Materials Science, NCSR "Demokritos", GR-15310 Ag. Paraskevi, Athens, Greece

Abstract

The electronic and magnetic and transport properties of ferromagnet/semiconductor (FM/SC) heterostructure systems have been studied by means of various band structure methods (LMTO, KKR-CPA, TB-KKR). As a structural model for our calculations periodic multilayer systems as well as half-infinite trilayer systems have been assumed, taking for the ferromagnet Fe and for the semiconductor GaAs or Ge.

Together with the profile of the spin and orbital magnetisation the magneto-crystalline anisotropy has been investigated in detail to check the relationship between the electronic magneto-crystalline anisotropy energy and the anisotropy of the orbital moment as proposed by van der Laan.

Making use of the Coherent Potential Approximation (CPA), the influence of interdiffusion at the Fe/GaAs interface within the multilayer system has been studied.

On the basis of the electronic structure calculations, the magnetic circular X-ray dichroism (MCXD) has been calculated for the L_3-edges absorption spectra of Fe, Ga and As in the near-edge regime (XANES).

The transport properties of FM/SC heterostructure systems were studied by making use of a relaxation time approach. The results were combined with data for the exchange coupling to give the conductivity as a function of an external magnetic field.

In addition to these model studies, first principle calculations of the conductance of FM/SC tri-layer systems have been made using the TB-KKR method in combination with the Landauer Büttiker formalism. Attention has been paid in particular to the influence of the spin-orbit coupling. It turned out that the TMR ratio can be reduced in a rather appreciable way by the spin-orbit coupling with the conductance of the anti-ferromagnetic configuration more influenced than the ferromagnetic one.

Kondo effect in quantum dots coupled to ferromagnetic leads

J. Martinek,[1,2,3] Y. Utsumi,[4] H. Imamura,[4] J. Barnaś,[3,5]
S. Maekawa,[2] J. König,[1] and G. Schön[1]

[1]Inst. für Theoretische Festkörperphysik, Univ. Karlsruhe, 76128 Karlsruhe, Germany
[2]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[3]Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland
[4]Graduate School of Information Sciences, Tohoku University, Sendai 980-8579, Japan
[5]Department of Physics, Adam Mickiewicz University, 61-614 Poznań, Poland

Abstract

We study the Kondo effect [1] in a quantum dot [2] which is coupled to ferromagnetic leads, and analyse its properties as a function of the spin polarization of the leads. The new key questions which emerge are: (i) does the Kondo effect survive and how does the spin-asymmetry affect the effect, (ii) how are the transport properties modified, and (iii) what is the ground state of the system? We analyzed these and related questions using scaling

arguments [3,4] and the equation of motion (EOM) technique [5]. The Kondo effect in transport through a quantum dot coupled to ferromagnetic leads is shown to be modified by the spin polarization of the electrodes and to have qualitatively new features as compared to the situation in a non-magnetic case [6]. Based on a poor man's scaling analysis we first show that the strong-coupling limit can still be reached in this case if an external magnetic field is applied. This is familiar from the Kondo effect in QDs with an even number of electrons [7,8], which occurs at finite magnetic fields, although the physical mechanism is different in the present case. We also analyze within an equation-of-motion (EOM) approach the nonlinear transport through the QD. We find that for parallel alignment of the lead magnetizations the zero-bias anomaly is split. This splitting can be removed by appropriately tuning the strength of an external magnetic field. In the antiparallel configuration of the lead magnetizations no splitting occurs at zero field in a symmetrical situation. A conceivable realization of proposed system might be carbon nanotubes, where the Kondo effect has been observed already, in contact to ferromagnetic leads. Alternatively one might use magnetic tunnel junctions with magnetic impurities in the barrier, spin-polarized STM or other molecular systems.

1. A. C. Hewson, *The Kondo Problem to Heavy Fermions,* Cambridge Univ. Press (1993).

2. L. I. Glazman and M.E. Raikh, JETP Lett. **47**, 452 (1988); T.K. Ng and P.A. Lee, Phys. Rev. Lett. **61** (1988) 1768.

3. P.W. Anderson, J. Phys. C **3** (1970) 2439.

4. F.D.M. Haldane, Phys. Rev. Lett. **40** (1978) 416.

5. Y. Meir, N.S. Wingreen and P.A. Lee, Phys. Rev. Lett. **66** (1991) 3048; N.S. Wingreen and P.A. Lee, Phys. Rev. B **49**, 11040 (1994).

6. J. Martinek *et al.*, cond-mat/0210006.

7. M. Pustilnik, Y. Avishai, and K. Kikoin, Phys. Rev. Lett. **84**, 1756 (2000); M. Eto and Yu.V. Nazarov, Phys. Rev. B **64**, 085322 (2001).

8. M. Pustilnik and L.I. Glazman, Phys. Rev. Lett. **85**, 2993 (2000); Phys. Rev. B **64**, 045328 (2001).

March 16, Afternoon I

Electrical spin injection via EuS-based magnetic tunnel barriers

A.T. Filip, C.J.P. Smits, J.T. Kohlhepp, H.J.M. Swagten, B. Koopmans,
and W.J.M. de Jonge

Dept. of Applied Physics, Eindhoven University of Technology, the Netherlands

Abstract

PbS is a narrow gap diamagnetic semiconductor that is well lattice-matched with EuS, suggesting EuS/PbS heterostructures as an attractive candidate for an all-semiconductor spin valve device. Here we discuss the experimental realization of electrical spin injection into PbS via EuS spin filters. Firstly, the barrier growth conditions were optimized by comparing structural (XRD and XPS), magnetic (SQUID) and (magneto)transport properties. High

temperature growth resulted in a reduction of number of defects, but led to an increase in surface roughness. Best barriers were obtained by a low temperature growth (200C), followed by an in-situ annealing step at 430C. Preliminary magnetoresistive data indicate spin accumulation in the PbS layer. We also discuss double barrier devices, where the expected magnetoresistance ratio depends not only on the injection and detection efficiency, but also on the ratio between the injection rate and the relaxation rate in the non-magnetic layer (PbS).

Highly efficient spin injection in ferromagnet/insulator /semiconductor tunnel junctions studied by the oblique Hanle effect

W. van Roy,[1] V. F. Motsnyi,[1] P. Van Dorpe,[1] V. I. Safarov,[2] G. Borghs,[1] and J. De Boeck[1]

[1]Imec, Kapeldreef 75, B-3001 Leuven, Belgium
[2]Universite Aix-Marseille II, Marseille, France

Abstract

The presentation will give an overview of our results on the electrical spin injection from a ferromagnetic contact through a tunnel barrier into a semiconductor LED between 4.2 K and room temperature, and on the use of the oblique Hanle effect to manipulate the spins and analyse their dynamics within the semiconductor. Due to the shape anisotropy of the ferromagnetic thin film contact, the electrons are injected with an in-plane spin. The circular polarization of a surface-emitting light emitting diode only carries information about the out-of-plane component of the electron spin. To convert between both we have introduced the oblique Hanle effect as a way to manipulate the spins inside the semiconductor. A small (< 0.5 T) external magnetic field is applied at an angle (typically 45 deg) with the sample surface, causing the spins to precess and creating a non-zero perpendicular spin component. The characteristic signature of this process allows us to clearly distinguish the spin injection signal from side effects such as the magneto-optical effects in the semitransparent magnetic contact. In addition, it enables the study of the spin dynamics within the semiconductor, and full determination of electron and spin lifetimes. Our workhorse samples consist of an (Al,Ga)As-GaAs LED structure grown by MBE, which is transferred through air to a sputter system where Al is deposited and oxidised to AlO_x in a controlled O_2 ambient, followed by the deposition of the semitransparent CoFe/NiFe/Cu magnetic contact. In addition we are investigating spin injectors based on half-metallic NiMnSb (grown epitaxially on a Schottky tunnel barrier) and the ferromagnetic semiconductor (Ga,Mn)As (grown on a Zener diode to convert the spin-polarized holes into electrons). In the $CoFe/AlO_x/$(Al,Ga)As structures we have demonstrated injected spin polarizations of 21% and 16% at 80 K and 300 K, resp. The spin polarization of the $CoFe/AlO_x$ interface as determined from TMR experiments is 40% and 30% at these two temperatures, indicating the high efficiency of the spin injection. The introduction of an oxide barrier allows us to use standard processing technology that is very robust (cf. transfer through air of the active interface) and generic (many semiconductor/ferromagnetic metal combinations are possible). From the bias dependence of the spin injection we can extract valuable information about electron thermalization effects inside the semiconductor, and about the optimum doping level in the semiconductor.

Spin-dependent ballistic electron transport through Fe/MgO/Fe from ab-initio Green function embedding

Daniel Wortmann[1], Stefan Blügel[1], and Hiroshi Ishida[2]

[1]Institut für Festkrperforschung, Forschungszentrum Jülich, Germany

[2]College of Humanities and Sciences, Nihon University, Japan

Abstract

An investigation of the Fe/MgO/Fe junction as a model system for tunnel-magneto-resistance (TMR) devices will be presented. We focus on the role of the electronic and geometric interface structure on the spin-dependent conductance by taking the interlayer relaxation at the Fe/MgO interface and the effect of a formation of interface FeO into account.

We apply a recently developed efficient method for calculating the conductance of ballistic electrons through an interface from first-principles using the embedding approach of Inglesfield. In our method the Landauer-Bttiker formula for ballistic transport is expressed in terms of quantities that are available in the embedded Green-function calculations. The embedding approach is implemented within the full-potential linearized augmented plane method as realized in the FLEUR code.

Materials for Spintronics: Electronic Structure of Correlated Half-Metals

W.M. Temmerman

Daresbury Lab, Daresbury, England

Abstract

A review is given of electronic structure of correlated half-metals based on transition metal oxide materials. In particular, $La_{0.7}Sr_{0.3}MnO_3$, $Ni_{.97}O$ and $Mn_{.97}O$ (a new class of half-metals), dilute magnetic semiconductors: Mn in GaN, GaP and GaAs, magnetite and double perovskites will be discussed. The electronic structure of these materials is investigated with the same bandstructure method: the self-interaction corrected local spin density (SIC-LSD). It is shown that the SIC-LSD accounts well for static correlations: it describes orbital order in $LaMnO_3$, it finds that the charge ordered state of Fe_3O_4 is more complicated than the Verwey ordered state and possibly also involving orbital order. Results will also be presented of a $La_{0.7}Sr_{0.3}MnO_3$(LSMO)/$SrTiO_3$ junction as a function of interface layer (either TiO_2 or MnO_2). It is found that for the MnO_2 interface the junction preserves the half-metallic character albeit with a reduced energy gap in the minority spin channel. Finally, it is found that tetragonal distortions of the O octahedra can readily change the Mn valency in LSMO.

Spin transport in semiconductor/ferromagnet hybrid structures

R. Jansen

MESA+ Research Institute, University of Twente, The Netherlands

Abstract

Taking full advantage of electron spin in spin-electronics will eventually require an intimate integration of ferromagnetic and semiconductor materials. While device concepts are emerging, the understanding of spin transport in such hybrid ferromagnet/semiconductor structures is still at its infancy. We have focused on transport of non-equilibrium, hot-electron spins, for which spin currents can be controlled and manipulated via the electron energy and momentum. A particularly useful device for that purpose is the spin-valve transistor, consisting of a metallic spin-valve base, sandwiched between a semiconductor emitter and collector. Using the spin-valve transistor, we address the relative importance of interface, volume and thermal scattering of hot electron spins, and present new insight into the sources of spin-asymmetry in hot-electron transport. From an application point of view, enhancing the output current of the transistor is desired. We demonstrate several routes to enhance the transfer ratio, culminating in an overall improvement by two orders of magnitude while preserving the low-field magnetic response above 200% at room temperature. We also briefly address transport in novel structures such as the magnetic tunnel transistor, as well as fully epitaxial transistors and diodes based on magnetic oxides.

Magnetic tunnel transistors: A source of highly spin polarized electron current

Stuart S.P. Parkin[1], Xin Jiang[1], Sebastiaan van Dijken[1], Roger Wang[1], Bob Shelby[1], Roger MacFarlane[1], Glenn Solomon[2] and James Harris[2]

[1]IBM Research Division, Almaden Research Center, San Jose, California 95120
[2]Solid State Photonics Laboratory, Stanford University

Abstract

We show that a magnetic tunnel transistor (MTT) provides a source of nearly 100% spin polarized electrons through spin filtering in ferromagnetic thin films. The MTT is comprised of a tunnel junction married to a semiconductor collector. Electrons are injected from a ferromagnetic or non-magnetic emitter across a tunnel barrier into a metallic base layer, comprised of one or more ferromagnetic layers, formed on GaAs. A Schottky barrier is formed at the base/semiconductor interface. The energy of the injected electrons is varied by applying a voltage across the tunnel barrier. When the electron energy exceeds the height of the Schottky barrier a collector current is measured. The collector current depends on the relative alignment of the magnetization of the ferromagnetic layers in the emitter and base layers. Magneto-collector current changes exceeding 3400% are observed at 77K. Features in the energy dependence of the collector current and the magneto-collector current can

be modeled in detail by assuming a significant spin-dependent broadening of the electron energy distributions through inelastic scattering in the baser layer plus substantial angular broadening of these distributions. Finally, we explore the spin polarization of the collector current in the GaAs collector by measuring the polarization of light emitted from a GaAs quantum well heterostructure on which the MTT is deposited through metal shadow masks.

Size-independent spin switching field using a synthetic ferrimagnet

K. Inomata[1,2], N. Koike[1], T. Nozaki[1], S. Abe[1] and N. Tezuka[1,2]

[1]Department of Material Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan, [2]CREST-JST

Abstract

Ferromagnetic nanostructures have been of growing scientific interest, mainly because these systems provide the basic magnetic architecture required to create spintronics such as magnetic random access memories (MRAMs) and spin transistors. Current efforts to manufacture high-density MRAMs using magnetic tunneling junctions (MTJs) require the production of both large-area arrays and cells scaled down to 100 nm dimensions. One difficulty in such scale devices is how to control the switching of the magnetization and attain a small switching field H_{sw}, because the demagnetizing field of the nanometer scale bits is significantly large, and leads to complex magnetic domain structures depending on the aspect ratio of the elements. Higher aspect ratio stabilizes single domain structure due to the magnetic shape anisotropy, but it brings the larger switching field, which hampers the development of high density spintronics devices. While, lower aspect ratio leads to the smaller switching field, but facilitates to produce multi-domain structures which are not suitable to spintronics devices.

We have proposed an element structure for reducing the switching field of nanometer scale devices, which is the synthetic ferrimagnet (SFM) consisting of antiferromagnetically coupled layers through a nonmagnetic layer[1-4]. This structure allows the magnetic flux to close creating less stray field, which reduces the magnetostatic coupling with close neighboring ferromagnetic layers. It is expected that SFM facilitates to form single domain structure even in the lower aspect ratio, and reduces the magnetostatic energy, resulting in reduced switching field of the nanometer scale elements. In this work the arrays of the SFM patterned bits consisting of $Co_{90}Fe_{10}(t_1$ nm$)/Ru(d$ nm$)/Co_{90}Fe_{10}(t_2$ nm$)$ and MTJs with a SFM free layer were successfully fabricated with micron to submicron sizes and different aspect ratios. Spin switching field H_{sw} and magnetic domain structure were investigated using magnetooptical Kerr effect (MOKE) and magnetic force microscopy (MFM) for the SFM bit arrays, respectively. It is demonstrated that the strongly antiferromagnetic coupled SFM with aspect ratio $k = 1$ creates size-independent H_{sw} down to submicron sizes fabricated, which is understood by zero demagnetization field for $k = 1$ and single domain structure, which was observed by MFM, while the H_{sw} for monolayers steeply increases with the reduced size below submicron. The switching field of MTJs with a SFM free layer was also investigated for $k = 1$ as a function of the junction size, which also showed size-independent H_{sw} down to

submicron sizes fabricated, and exhibited a lower H_{sw} than that of the conventional MTJs with a single free layer.

The size-independent switching field obtained for the SFM with $k = 1$ demonstrates the predominance of the SFM for spintronics devices, requiring a low switching field and stabilized single domain structure for small bit sizes. MTJ with a SFM free layer may be promising for high bit density MRAMs, because TMR of the MTJ is the same as that of the conventional MTJ using a single free layer, in addition to the reduced switching field.

References:

1. K. Inomata, S. N. Okuno and Y. Saito, Japanese Patent Kokai (1997).

2. K. Inomata, T. Nozaki, N. Tezuka and S. Sugimoto, Appl. Phys. Lett. **82**, 310 (2002).

3. N. Tezuka, E. Kitagawa, K. Inomata, S. Sugimoto, N. Kikuchi and Y. Shimada, J. Magn. Magn. Mater. **240**, 294 (2002).

4. N. Tezuka, N. Koike, K. Inomata and S. Sugimoto, Appl. Phys. Lett., in-press

March 17, Morning I

Electronic transport through single molecules[*]

H. v. Löhneysen[1,2]

[1]Physikalisches Institut, Universität Karlsruhe, D-76128 Karlsruhe, Germany
[2]Forschungszentrum Karlsruhe, Institut für Festkörperphysik,
D-76021 Karlsruhe, Germany

Abstract

The electronic transport through molecules is an active area of research. In order to establish that one is indeed dealing with single molecules, we have investigated transport through two types of conjugated molecules which differ by their spatial symmetry. Mechanically controlled break junctions have been used to couple thiol end groups of the molecules to two gold electrodes. The current voltage characteristics (IVs) of the metal-molecule-metal system reflect the spatial symmetry of the molecules with respect to the direction of current flow. We hereby unambiguously detect an intrinsic property of the molecule and in addition are able to distinguish the influence of both the molecule and the contact to the metal electrodes on the transport properties of the compound system. Fluctuations in the IVs are a manifestation of the level spacings of the system electrode-molecule-electrode, which depend crucially on the bonding between thiol end groups and Au electrodes.

[*]Work done in collaboration with J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, Forschungszentrum Karlsruhe, Institut für Nanotechnologie.

Ab-initio study of the magnetoresistance effects in magnetic nanocontacts

Alexei Bagrets[1,2], Nikos Papanikolaou[2,3], and Ingrid Mertig[2]

[1]Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle, Germany
[2]Martin-Luther-Universität Halle, Fachbereich Physik, D-06099 Halle, Germany
[3]Institute of Materials Science, NCSR "Demokritos", GR-15310 Athens, Greece

Abstract

We present *ab-initio* calculations of transport properties of metallic atomic sized nanocontacts. The nanocontacts were modelled by short atomic chains of Co, Cu, Al, and Si embedded between two semi-infinite magnetic Co leads. The first-principle screened Korringa-Kohn-Rostoker (SKKR) method was used to calculate the electronic properties of the systems. Both Co leads and atomic chains are treated on the same footing without model parameters. The Landauer formalism adapted for the SKKR method was used to calculate conductance $G(E)$ and magnetoresistance (MR) as a function of the electron energy E in the region -1.5eV ... $+1.5$eV nearby the Fermi energy. Magnetic leads result in a complicated energy dependence of the minority conductance both for magnetic Co chains and chains formed from nonmagnetic (Cu, Al, Si) atoms. The conductance curves $G(E)$ reproduce peculiarities of the local density of states of the atoms forming the chains. MR is sensitive to geometry and chemistry of the constriction. MR ratios of 20-50% are obtained for Co, Cu, Al and Si chains between Co leads at the Fermi energy. MR ratios even higher than 50% are obtained for Cu, Al and Si chains at energies about -0.3eV below the Fermi level.

Electrical spin injection and coherent spin dynamics in semiconductor heterostructures

Y. Ohno[1,2], M. Kohda[1], H. Sanada[1], K. Morita[1,3], C.Y. Hu[1,2], F. Matsukura[1], and H. Ohno[1,3]

[1]Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[2]CREST, Japan Science and Technology Corporation
[3]Ohno Semiconductor Spintronics Project, ERATO, Japan Science and Technology Corporation

Abstract

In recent years, spin related phenomena in semiconductors have attracted much attention from both viewpoints of physics and applications. To realize spintronics devices based on magnetic and/or nonmagnetic semiconductor heterostructures, injection and transfer of spin-polarized electrons and storage and manipulation of the electronic spin states are key technologies.

In this workshop, we first discuss electrical electron spin injection in a ferromagnetic p$^+$-(Ga,Mn)As/non-magnetic n$^+$-GaAs tunnel junction with a light emitting diode (LED)[1]. By applying a reverse bias to the p$^+$-(Ga,Mn)As/n$^+$-GaAs junction (forward bias to the LED), we observed clear hysteresis in electroluminescence (EL) polarization, indicating successful injection of spin-polarized electrons from the valence band of (Ga,Mn)As into the conduction band of GaAs.

We then present a study on transport of photoinjected spins in GaAs under an electric field studied by time-resolved photoluminescence measurements[2]. At low temperatures, the spin polarization after drift transport of $4\mu m$ is found to decrease as the applied electric field E increases to a few kV/cm, and it disappears when E exceeds 3 kV/cm. The origin of the field-dependent spin relaxation is discussed based on D'yakonov-Perel' (DP) spin relaxation mechanism.

Finally, to manifest coherent spin dynamics in semiconductor heterostructures, we employed GaAs/AlGaAs quantum well (QWs) grown on a GaAs (110) substrate with n-doping, in which a predominant spin scattering mechanism (DP interaction) for conventional (100) QWs is substantially suppressed[3] and the spin relaxation time τ_s in n-modulation doped (110) QWs is found to reach 10 nanosecond order even at room temperature. The optically pumped two-dimensional electron gas with long τ_s is shown to be a powerful tool for manipulation of nuclear spin. Using optical Larmor magnetometry, we find that nuclear spin can be polarized along or against the applied magnetic field, depending on field polarity and tilting of the sample with respect to the optical pump beam. Periodic optical excitation of the quantum-confined electron spin reveals a complete spectrum of optically induced and quadrupolar-split nuclear resonances [4]*.

*Work done in collaboration with D. D. Awschalom, G. Salis, D. T. Fuchs, and J. M. Kikkawa at University of California, Santa Barbara.

1. M. Kohda, Y.Ohno, K. Takamura, F. Matsukura and H. Ohno, Japanese Journal of Applied Physics **40**, L1274 (2001).

2. H. Sanada, I. Arata, Y. Ohno, Z. Chen, K. Kayanuma, Y. Oka, F. Matsukura, and H. Ohno, Applied Physics Letters **81**, 2788 (2002).

3. Y. Ohno, R. Terauchi, T. Adachi, F. Matsukura, and H. Ohno, Physical Review Letters **83**, 4196 (1999).

4. G. Salis, D.T. Fuchs, J.M. Kikkawa, D.D. Awschalom, Y. Ohno and H. Ohno, Physical Review Letters **86**, 2677 (2001).

March 17, Morning II

Half-metallic zinc-blende compounds

Ph. Mavropoulos, I. Galanakis, and P. H. Dederichs

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

Abstract

Motivated by recent realisation of ferromagnetic zinc-blende CrAs and CrSb compounds by molecular beam epitaxy [1], we present systematic first-principles calculations for ordered zinc-blende compounds of the transition metal elements V, Cr, Mn with the *sp* elements N, P, As, Sb and S, Se, Te. These compounds exhibit a half-metallic behaviour over a wide range of lattice constants. We discuss the origin and trends of the half-metallic behaviour and the strong similarities to analogous dilute magnetic semiconductors. Based on calculations of the equilibrium lattice constants, we discuss the possibility to grow these half-metallic systems on suitable semiconductor substrates and identify several systems with a lattice mismatch smaller than 2%: VAs/GaAs, VSb/InAs, VSb/GaSb, CrAs/GaAs, CrSb/InP, CrSb/InAs, CrSb/GaSb, CrSe/CdS, CrTe/CdSe, and CrTe/ZnTe.

Moreover, we examine multilayered structures of these half-metals with semiconductors. We find that half-metallicity is preserved at the interface (and thus throughout the multilayer), and that the local magnetic moments do not change appreciably.

[1] H. Akinaga, T. Manago, and M. Shirai, Jpn. J. Appl. Phys. **39**, L1118 (2000).

Residual resistivity in (Ga,Mn)As alloys

Ilja Turek,[1,2,4] Josef Kudrnovský,[3,4] Václav Drchal,[3,4] and Peter Weinberger[4]

[1]Institute of Physics of Materials AS CR, 61662 Brno, Czech Republic

[2]Dept. of Electronic Structures, Charles Univ., 12116 Prague, Czech Republic

[3]Institute of Physics AS CR, 18221 Prague, Czech Republic

[4]Center for Comput. Materials Science, TU Vienna, 1060 Vienna, Austria

Abstract

The residual resistivity in diluted (Ga,Mn)As magnetic semiconductors is calculated from first principles using the Kubo-Greenwood linear response theory. The electronic structure is described within the local spin density approximation using the tight-binding linear muffin-tin orbital method in the atomic sphere approximation. The chemical and magnetic disorders of the alloys are treated in the coherent potential approximation. Particular attention is paid to the role of native defects like As-antisites and Mn-interstitials as well as of the local moment disorder of Mn atoms.

The order of magnitude of the calculated resistivities compares reasonably well with available experimental data. The calculated resistivity of alloys with a fixed concentration of As-antisites decreases with increasing Mn-content, in clear contrast to conventional metallic alloys. This effect is due to the increase of number of carriers. For the same reason, the resistivity of alloys with a fixed Mn-content increases with increasing concentration of As-antisites. The resistivities differ significantly for the cases with parallel and antiparallel orientations of magnetic moments of the substitutional and interstitial Mn atoms. The calculated resistivities are strongly correlated to the alloy Curie temperatures evaluated in the mean field approximation for a classical Heisenberg Hamiltonian.

First principle study of the electronic properties of ultrathin Fe layers on NiO

Leonardo Di Giustino, Valerio Bellini and Franca Manghi

INFM-National Research Center on nanoStructures and bioSystems at Surfaces (S3) and Dipartimento di Fisica, Università di Modena, Via Campi 213/A, I-41100 Modena, Italy

Abstract

The study of antiferromagnetic-ferromagnetic systems, such as NiO/Fe, has recently drawn much attention for the phenomenon of the exchange-bias that finds today a vast application in the development of the new generation spin-based nanotechnologies. In order to understand their characteristic properties it is of fundamental interest the analysis of the interplay between magnetic interactions driven by the exchange coupling mechanism and the structural characterization of the interface region between the two magnetic materials. With this backdrop in mind, we have investigated -by means of the linearized augmented plane wave (LAPW) method within the framework of density functional theory (DFT)- the ground state electronic properties of ultrathin Fe layers on NiO (001) substrate. We have considered different absorption sites for the iron on the NiO surface and the effects of Fe oxidation, and consequent Ni reduction, on the magnetic properties. The stability of several magnetic configurations, i.e. the magnetic ordering of the two elements at the interface, has been discussed and it has found to be intimately related to the level of oxidation at the interface region. Accurate total energies calculations performed for the relaxed structures indicates a tendency for iron to drag oxygen atoms from the NiO layers, and to order antiferromagnetically.

Ballistic spin injection from Fe into ZnSe and GaAs

O. Wunnicke, Ph. Mavropoulos, R. Zeller, and P.H. Dederichs

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

Abstract

We have investigated the ballistic spin injection from Fe into the semiconductors ZnSe and GaAs by means of an *ab initio* method. The results show a very high spin polarization up to 99% for the [001] growth direction but relatively smaller spin polarizations for the [111] and [110] direction. The origin of the high spin polarization for the [001] direction can be traced back to the different symmetries of the majority and minority spin wave functions. This symmetry-enforced spin polarisation is absent for the other investigated directions, i.e., the [111] and [110] direction.

The calculation of the ground state properties is based on the density functional theory within the local density approximation and uses the screened KKR-Green's function method.

The conductance is calculated by the Landauer-Büttiker formula in a Green's function description. We have investigated three different injection processes: (*i*) the injection of hot electrons directly into the conduction band of the semiconductor, (*ii*) the injection of thermal electrons at the Fermi energy without and (*iii*) with including a Schottky barrier at the interface.

If a Schottky barrier is included at the interface, new effects from resonant interface states in the minority band can come in. In principle they could dominate the tunnel current and can even change the sign of the current polarization, although in the present calculations their influence is modest. We have calculated the interface resistance of the Schottky barrier in the (001) orientation as an input value for the analytical models of spin injection through a tunneling barrier proposed independently by Rashba and Fert *et al.* By this we can roughly estimate the required thickness of the Schottky barrier to be 70Å for Fe/ZnSe and 100Å for Fe/GaAs(001).

Finally, we have added a second Fe lead for the detection of the injected current. We observe interesting conductance oscilations due to the quantum well states occuring, and calculate extremely high magnetoresistance values, close to the ideal 100%.

"Polaronic" modes in nano-magnetomechanical systems

Alexey A. Kovalev,[1] Gerrit E. W. Bauer,[1] and Arne Brataas[2]

[1]Department of NanoScience, Delft University of Technology,
2628 CJ Delft, The Netherlands
[2]Department of Physics, Norwegian University of Science and Technology,
N-7491 Trondheim, Norway

Abstract

A nano-magnetomechanical system consisting of a cantilever and a thin magnetic film is predicted to display novel magnetovibrational modes. Due to mode mixing of mechanical and magnetization degrees of freedom the coherent magnetization dynamics has two or zero resonances instead of a single one. Firstly this leads to line splittings in the ferromagnetic resonance secondly, in the crossing region of the pure magnetic and mechanical modes a "polaronic" gap opens. In this gap magnetization oscillations decay very fast and absorption of external rf magnetic field is suppressed. The mentioned effects can be used for sensors and actuators as well as for measuring characteristics of small magnets and cantilevers.

Figure 1. A nano-magneto-mechanical cantilever supporting magneto-vibrational modes. On dielectric substrate (such as Si) a single-domain ferromagnetic film is deposited at the free end.
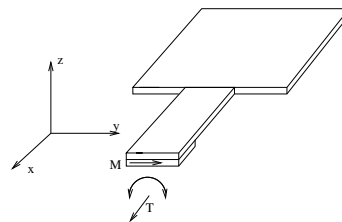
Relativistic effects in the transport properties of ferromagnetic-semiconductor-ferromagnetic (FM/SC/FM) trilayer systems

V. Popescu,[1] H. Ebert,[1] R. Zeller,[2] N. Papanikolaou,[3] and P. H. Dederichs[2]

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

[2] Inst. für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany

[3] Institute of Materials Science, NCSR "Demokritos", GR-15310 Ag. Paraskevi, Athens, Greece

Abstract

We report results of calculations on the electronic, magnetic and transport properties of As-terminate Fe/GaAs/Fe trilayer systems that have been obtained on the basis of Spin-Polarised Relativistic Multiple Scattering Theory (TB-SPR-KKR).

The transport properties of this system are investigated by means of the Landauer-Büttiker formalism. The tunneling conductance and the magneto-resistance are calculated on a relativistic level. Model calculations allowed us to gradually manipulate the strength of the spin-orbit coupling and to investigate in detail its quantitative and qualitative influence on the spin-dependent transport.

Our investigations include also a set of spin-spiral structures, which allowed us to extract averaged interlayer exchange parameters and their dependence on the width of the semiconductor spacer. The dependence of the conductance and magnetoresistance on the width of the semiconductor spacer and the relative angle between the moments of adjacent Fe-layers enabled us to determine a qualitative dependence of the electronic transport on an external magnetic field.

Electronic structure and magnetic properties of $M_n/Cu_m/M_n$ metallic multilayers with M=Fe, Co and Ni

P. Vlaic, M. Alouani, H. Dreyssé, O. Bengone[*]

Institute de Physique et Chimie des Matériaux de Strasbourg, UMR 7054 du CNRS, 23, rue du Loess, F-67037 Strasbourg, France

[*]Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden

Abstract

Electronic structure calculations are performed for fcc (001) $M_n/Cu_m/M_n$ (M=Fe, Co and Ni) and bcc (001) $Fe_n/Cu_m/Fe_n$ trilayers (n, $m=$ integer numbers of atomic interlayers) using a first-principle tight-binding linear muffin-tin orbitals method (TB-LMTO) combined with coherent potential approximation (CPA) in order to describe the disorder effects such

as interdiffusion at interfaces. The results show that the iron magnetic moments in bcc $Fe_n/Cu_m/Fe_n$ trilayers are enhanced at the interface compared with the bulk value while only small variations are obtained in the case of fcc $M_n/Cu_m/M_n$ trilayers (M=Co and Ni). Different types of magnetic couplings are analysed as a function of M or Cu thickness in order to predict the most stable configurations.

Quantum theory of shuttling instability

Tomáš Novotný[1,2], Andrea Donarini[1], and Antti–Pekka Jauho[1]

[1]Mikroelektronik Centret, Technical University of Denmark, Ørsteds Plads, Bldg. 345 east, DK-2800 Kgs. Lyngby, Denmark
[2]Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic

Abstract

A quantum theory of the shuttle instability in electronic transport through a Coulomb blockade nanostructure with a mechanical degree of freedom is presented. We identify a cross-over from the tunnelling to the shuttling regime using a phase space formulation in terms of the Wigner function, thus extending the previously found classical results to the quantum domain. We also discovered a new dynamical regime, where the shuttling is driven exclusively by the quantum noise. Further development of the presented formalism will allow to model spintronics devices containing a mechanical degree of freedom.

Spin-valve effect in a mesoscopic double-barrier junction

Wojciech Rudziński,[1] and Jozef Barnaś,[1,2]
[1]Department of Physics, Adam Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland
[2]Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17, 60-179 Poznan, Poland

Abstract

Spin-dependent electronic transport through a single-level quantum dot coupled to two ferromagnetic leads is studied theoretically in the sequential tunnelling regime. Transport characteristics of the device, including occupation numbers, electric current, spin polarization of the current as well as the tunnel magnetoresistance are calculated in the framework of the master equation method for both symmetrical and asymmetrical junctions. In particular, we found that the diode-like behaviour, found previously [1, 2] for the collinear magnetic (parallel and antiparallel) configurations of the junction with one electrode being half-metallic, is significantly suppressed for canted magnetic configurations. The transport characteristics have also been examined as a function of temperature. Generally, in the case of symmetrical

junctions the thermal distribution of electrons gives rise to current suppression, whereas in asymmetrical devices with one half-metallic electrode, the thermal distribution diminishes the current blockade.

[1] B.R. Buka, Phys Rev. B 62, 3186 (2000);

[2] W. Rudziski and J. Barnas, Phys. Rev. B 64, 085318 (2001).

Spin injection and accumulation in a mesoscopic metal island

M. Zaffalon and B.J. van Wees

Department of Applied Physics and Material Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

Abstract

In a spin valve experiment, the basic idea is to create a spin imbalance into a non magnetic metal or semiconductor. Spin injection from FM electrodes into a diffusive paramagnetic metal has been shown both for clean contacts (FM/N) and with tunnel barriers (FM/I/N)[1]. As the Al strip is much longer than the spin flip length, the spins diffuse in the metal and can "leak out", and eventually relax, undetected.

Following this work, we study spin injection into an island whose size (500×500 nm^2) is smaller than the spin relaxation length $\lambda_{sf} \approx 1\mu m$. This results in the spin imbalance being uniform in the island. In this respect, the system under study is 0-dimensional.

Four cobalt electrodes are connected to the island: this allow us to separate the voltage probes from the current path. By sweeping an externally applied magnetic field, we are able to change the magnetisation direction of the current electrodes from parallel to antiparallel. Only in the antiparallel case one observes spin accumulation. We observe a spin dependent resistance of 0.3 Ω, which is about 25 times larger than previously observed.

The electronic spin lifetime can be directly determined in a spin precession measurement. We develop for the spin signal in the island, a 0-dimensional approximation. By allowing for non-collinear magnetisation of the electrodes, our model accounts for the asymmetry of the spin precession data at room temperature. We find the spin relaxation time to be $\tau_{sf} = 60 \pm 10$ ps.

[1] F.J. Jedema *et al.*, Nature **410**, 345 (2001), F.J. Jedema *et al.*, Nature **416**, 713 (2002)

Interface resistances from first principles

M. Talanana[1], M. Zwierzycki[1], K.Xia[2], P.J. Kelly[1], and G.E.W. Bauer[3]

[1]Faculty of Applied Physics and MESA$^+$ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

[2]State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, China

[3]Department of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Abstract

The open 3d shells of the transition metal atoms used to make magnetic multilayers give rise to complex band structures which have to be taken into account in any quantitative estimation of the interface scattering whose spin-dependence determines the remarkable transport properties of these structures. Using the TB-LMTO surface Green's function method we study a number of metallic and hybrid (metal/semiconductor) interfaces and interpret their transmittivity in terms of the electronic structures of the component materials. The efficiency of the TB-LMTO method allows us to treat disordered layers using large lateral supercells and allows us to unravel the contribution of various factors to the final transmission.

High order finite difference method for calculating electronic transport

Petr A. Khomyakov, Geert Brocks, and Paul J. Kelly,
Computational Materials Science, Faculty of Applied Sciences, MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands.

Abstract

Nanoelectronics, where devices consist of single molecules and atomic scale nanowires, is a topic of considerable interest at present. Coherent electron transport in such systems can be expressed as a quantum mechanical scattering problem. We propose a computational method to solve this scattering problem that is based upon first-principles density functional calculations. The states that propagate from one macroscopic metal electrode, through a single molecule or nanowire, to a second metal electrode, are calculated explicitly on a real space grid. The microscopic structure of the whole system including the electrodes is taken into account, using pseudopotentials to represent the atoms. The conductance is calculated using the Landauer-Büttiker formalism. We present first computational results of our method applied to electron transport in a model system.

Spin-injection through an Fe/InAs interface

M. Zwierzycki[1], K. Xia[2], P. J. Kelly[1], G. E. W. Bauer[3], and I. Turek[4]

[1]Faculty of Applied Physics and MESA$^+$ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[2]State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, China
[3]Department of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands
[4]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, CZ-616 62 Brno, Czech Republic

Abstract

The spin-dependence of the interface resistance between ferromagnetic Fe and InAs is calculated from first-principles for specular and disordered (001) interfaces. Because of the symmetry mismatch in the minority-spin channel, the specular interface acts as an efficient spin filter with a transmitted current polarisation between 98 an 89%. The resistance of a specular interface in the diffusive regime is comparable to the resistance of a few microns of bulk InAs. Symmetry-breaking arising from interface disorder reduces the spin asymmetry substantially and we conclude that efficient spin injection from Fe into InAs can only be realized using high quality epitaxial interfaces.

4   News from the RTN2 ("f-electrons")

"Ab initio computation of electronic properties of f-electron materials"

4.1   RTN2 Position Announcements

DEPARTMENT OF PHYSICS
UPPSALA UNIVERSITY, SWEDEN

One Post-doctoral Position

Theoretical Magnetism:
Electronic Structure of f-electron Materials

Applications are invited for one post-doctoral position funded by the European Research Training Networks, **Psi-k f-electron**: '*Ab-initio Computation of Electronic Properties of f-electron Materials*'

The position is available for a period of 2 years starting first half of 2003. Extension is possible.

The applicants must comply with the RTN rules for network employment of young scientists: The applicants should hold a Ph.D. degree or equivalent in Physics or Chemistry, be aged 35 or younger, and should have some experience in computational Condensed Matter Theory. They must be of European Union nationality, or from one of the Associated Nations, or have resided in an EU country for the last five years or longer.

The work tasks involve applications of present computer codes to solid systems of high current interest as well as development of improved computer codes. The projects are collaborations in international teams and some travel activity between the research centers involved must be foreseen. More detailed information concerning the project can be obtained upon request.

Applicants must submit a curriculum vitae, a description of scientific accomplishments, and a list of publications (all in 4 copies), and 3 copies of publications to be considered in the evaluation.

Salary as agreed between the Swedish Ministry of Finance and the Confederation of Professional Unions.

Applications should be addressed to

Olle Eriksson
The Department of Physics

Uppsala University

Ångstrom laboratory

Box 530

Uppsala

Sweden

The deadline for receipt of all applications material is June 30, at 12:00 noon.

For further information, contact

Olle Eriksson

Phone: (+46)-(0)18-4713625,

Email: olle.eriksson@fysik.uu.se

Information about the Department can also be found on http://www.uu.se.

4.2 RTN2 Workshop Announcements

4.2.1 RTN2 Workshop on "The Physics of f-electron Solids"

October 24-25, Århus, Denmark

The workshop will focus on new developments in the theory of f-electron systems. While organised in the framework of the RTN2 network 'Psi-k: f-electrons', the workshop will be open to anyone interested. Details of the scientific program, etc., will follow in the next Psi-k Newsletter (August 2003 issue). Please, notify us, if you want to be on the mailing list.

Organisers:

Axel Svane
Department of Physics and Astronomy, University of Århus, Denmark
Phone: +45-8942-3678, Fax: +45-8612-0740,
`svane@phys.au.dk`

Walter Temmerman
Daresbury Laboratory, UK
Phone: +44-1925-603227, Fax: +44-1925-603634,
`W.M.Temmerman@dl.ac.uk`

4.3   Reports on RTN2 Meetings/Workshops

4.3.1   Report on 'Actinide Laboratory User Meeting'

Highlights in f-electron theory
31 March - 1 April 2003, Karlsruhe, Germany

The Institute for Transuranium Elements held an 'Actinide Laboratory User Meeting on f-electron Theory' from 31st March to 1st April. The focus was on computational theory which naturally led to both conventional and unconventional approximations to density functional theory, appropriate to 5f electrons. P. Oppeneer (Leibnitz-Institute, Dresden) used conventional band structure calculations to investigate the electronic structure of the newly discovered plutonium superconducters and M. Komelj (Jozef Stefan Institute, Ljubljana) described recent calculations which suggest magnetic moment formation at the surface of α-uranium.

The valence of actinides in actinide compounds and its relationship to localization of the 5f electrons may be investigated using the self-interaction correction for localized 5f electrons as described by A. Svane (Institute of Physics and Astronomy, University of Aarhus). W. Temmerman (Daresbury Laboratory) explained how the self-interaction correction may also be used to study orbital and charge ordering. Another unconventional approximation, applied to the δ-Pu, in which some of the 5f electrons were localized and some delocalized was described by O. Eriksson (Institute of Physics, Uppsala University).

The most advanced approach to δ-Pu, which has an anomalous lack of any magnetic response, lattice constant and thermal expansion, is dynamic mean field theory and G. Kotliar (Physics Deparment, Rutgers University) described its application. Both the anomalous lattice constant and anomalous thermal expansion can be explained and it is argued that the absence of magnetic response is due to the Kondo effect.

The phenomenon of orbital magnetism in actinide compounds was treated by M. Brooks (Institute for Transuranium Elements, Karlsruhe) with particular emphasis on US and UFe_2 where it has proven difficult to describe the magnetism correctly within the local spin density approximation. H. v. Löhneysen (Physikalisches Institute, Karlsruhe) magnetic instabilties in cerium and uranium compounds, in particular non-Fermi liquid behaviour and quantum phase transitions. B. Johansson (Institute of Physics, Uppsala University) provided an historical perspective on actinide theory.

In an evening round table session visiting theorists showed some interest in recent experiments at the Institute for Transuranium Elements, including superconductivity in Plutonium compounds and Americium under pressure. H. v. Löhneysen led a discussion of the discovery of Pu superconductivity and F. Wastin (Institute for Transuranium Elements, Karlsruhe) gave a detailed description of this work in the institute. Also mentioned, and this was emphasised by

B. Johansson in his summary, was that research on actinide surfaces, thin films and multilayers is likely to become extremely interesting.

Program

Monday, 31st

14h00-14h45
G. van der Laan: 'Core-level photoemission to measure the 5f localization in actinides'

14h45-15h30
G. Kotliar: 'Applications of dynamical mean field theory to actinide materials'

15h30-16h00 Coffee

16h00-16h40
B. Johansson: 'High pressure studies of Am, AmCm alloys and PuCoGa5'

16h40-17h20
A. Svane: 'Total energy calculations of actinides using self-interaction corrections'

17h20-18h00
M.S.S. Brooks: 'Magnetic Moment composition in itinerant f-electron systems'

19h00-20h30 Dinner

20h30 Round Table "Perspectives"
G. H. Lander, F. Wastin, B. Johansson, H. v. Löhneysen, G. Kotliar

Tuesday, 1st

08h30-09h15
H. v. Löhneysen: 'Magnetic instabilities in f-electron systems'

09h15-10h00
M. Komelj: 'Prediction of a surface magnetic moment in α-uranium'

10h00-10h30 Coffee

10h30-11h10
P. M. Oppeneer: 'Fascinating actinide materials - Recent electronic structure investigations'

11h10-11h50
W. M. Temmerman: 'Localized states and valencies in Rare Earth's and Transition Metal

Oxides'

11h50-12h30
O. Eriksson: 'Properties of actinide elements'

12h30-13h00
Summary: G. H. Lander, B. Johansson

13h00 Lunch

Abstracts

Core-level photoemission to measure the 5f localization in actinides

G. van der Laan

Daresbury Laboratory, Warrington WA4 4AD, U.K.

In actinide metals the outer s and d electron orbitals are broad and overlap strongly and therefore show a metallic behavior. Conversely, the 5f orbitals which have a smaller radius have a more atomic-like behavior. In the actinide series the lightest elements have metallic-like f electrons, whereas the heavier actinides have atomic-like f electrons. As the atomic number of the nucleus increases, the attractive electrostatic interaction increases, pulling the f electrons closer to the atom. This causes the shape of the f orbital to change from overlapping to non-overlapping. The f orbitals are more spatially extended in the localized. In the actinides the transition occurs midway through the series between Pu and Am. In the lanthanides where the 4f orbitals are less spatially extended than the 5f in the actinides, the transition occurs in Ce. In lanthanides high pressure gives an increased overlap leading to a delocalization.

The physics of f electron systems at finite temperature is dominated by the phenomenon of f electrons fluctuating between different configurations. This has been impossible so far to include in the electronic methodology of a one-electron mean-field description. Pu is considered to be the most complex and anomalous elements in the periodic table. The phase diagram of Pu metal has seven allotropes, some with very complex crystal structures not found in other metals, such as alpha-Pu (the low-temperature phase) which has a complex monoclinic structure, whereas on the other hand delta-Pu has a simple face-centered cubic (fcc) structure. The delta-phase which is stable at ambient pressure and around 600 to 700 K has a 25 % larger atomic volume than the alpha-phase.

Results of Anderson impurity calculations will be presented for alpha and delta Pu and thin films of Pu with different thicknesses and compared to recent experimental results [1,2]. The 4f core-level photoemission spectra display a screened and an unscreened peak that can be used to measure for the degree of localization. An increased localization (more atomic-like) leads to decreased overlap which leads to a volume increase. There is a com-

petition between localization (electron-electron interaction) and delocalization (kinetic energy). The many-body crystal wavefunction has to reduce to many-body atomic wavefunctions as lattice spacing is increased. Such a strongly correlated electron system can be studied by Anderson impurity model (AIM) or dynamical-mean field theory (DMFT). In these models intra-atomic Coulomb interaction and hybridization are considered at the same footing. Correlation effects depend on the lattice phase. For instance, when the distance between the atoms is small, the correlation effects may not be so important, since the hybridization, and consequently the bandwidth becomes large.

References

[1] J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, D.K. Shuh, G. van der Laan, D.A. Arena, and J.G. Tobin, Surf. Sci. 499, 141 (2002).

[2] T. Gouder, L. Havela, F. Wastin, and J. Rebizant, Europhys. Lett. 55, 705 (2001).

Applications of dynamical mean field theory to actinide materials

G. Kotliar

Physics Department and Center for Materials Theory, Rutgers University

Dynamical Mean Field Theory, is a rapidly developing technique, which can treat materials where the electrons straddle a localization delocalization boundary. We will discuss the current state of the method, and how it has given some qualitative insights into the delta to epsilon transition in Pu. We will also discuss some qualitative ideas as to the origin of superconductivity in Am.

High pressure studies of Am, AmCm alloys and PuCoGa5

B. Johansson

Department of Physics, Condensed Matter Theory Group, Box 530, SE-751 21 Uppsala, Sweden

Density-functional electronic structure calculations have been used to investigate the high pressure behavior of Am, AmCm alloys and PuCoGa5. 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). The results are consistent with a Mott transition; the 5 f electrons are delocalized and bonding on the high density side of the transition and chemically inert and non-bonding (localized) on the other. Theory compares rather well with recent experimental data which implies that electron correlation effects are reasonably modeled in our orbital polarization scheme.

Total energy calculations of actinides using self-interaction corrections

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

[1] Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus, Denmark

[2] Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, U.K.

The self-interaction corrected local-spin-density method is applied to actinide systems. The method allows the first-principles comparison of scenarios with different valency of the actinide ion. Systems studied comprise the elemental metals, the monopnictides and monochalcogenides, as well as UX3, with X=Rh, Pd, Pt, Au. While the scheme correctly describes valency transitions in actinides, the magnetic properties continue to be a problem.

Magnetic moment composition in itinerant f-electron systems

M.S.S. Brooks

European Commission, Joint Research Center, Institute for Transuranium Elements, D-76125 Karlsruhe, Germany

The local spin density approximation fails when the orbital contribution to magnetism is important, as in magnetic actinides, since the approximate treatment of exchange is not orbital dependent. An orbital dependent, but parameter free, theory uses exchange integrals for a screened Coulomb interaction (SCI) with the Thomas-Fermi wave vector expressed in terms of the total electron density. We report application of this approximation to US and UFe2. For both US and UFe2 the measured (neutron diffraction) magnetic amplitude and total magnetic moment are reproduced almost exactly.

Magnetic instabilities in f-electron systems

H. v. Löhneysen

Physikalisches Institut, Universität Karlsruhe und Forschungszentrum Karlsruhe, Institut für Festkörperphysik

Metallic f-electron systems, by virtue of the competition between Kondo effect and RKKY interaction, offer the unique opportunity of studying transitions between different magnetic groundstates, viz. strongly enhanced Pauli paramagnet vs. long-range magnetic order. At the magnetic instability, pronounced non-Fermi liquid behavior is observed which is interpreted as arising from an underlying quantum phase transition. We will discuss scenarios for the microscopic origin of the non-Fermi liquid behavior, as inferred from inelastic neutron scattering. Special attention will be given to the systems CeCu6-xAux and UCu5-xPdx.

Prediction of a surface magnetic moment in alpha-uranium

N. Stojic[1,2], J.W. Davenport[1], M. Komelj[3] and J. Glimm[1,2]

[1] Brookhaven National Laboratory, Upton NY 11973-5751, U.S.A.

[2] Stony Brook University, Stony Brook, NY 11794-3381, U.S.A.

[3] Joef Stefan Institute, Jamova 39, Ljubljana SI 1000, Slovenia

Recently, there has been an increased interest in first-principle calculations of actinides as well as in finding the materials which display surface magnetism. Uranium would appear to be a possible candidate since there is a rather large change in density of states from surface to bulk, a comparatively modest expansion of lattice leads to a spontaneous moment in the bulk and it is near the transition (that occurs beyond plutonium) in which the 5 f electrons become localized. Furthermore, many U alloys are magnetic, indicating the possible presence of a nearby magnetic instability.

We have explored the possibility for magnetism in uranium within the framework of the density functional theory and the generalized-gradient (GGA) as well as the local-spin-density (LSDA) approximations for the exchange-correlation potential. We have applied the full-potential linearized-augmented-plane-waves (FLAPW) method with a fully-relativistic description of the core and a scalar- relativistic description of the valence states. In addition, the spin-orbit coupling has been included as a perturbation for the valence states.

The calculations have been done using the supercell technique for the orthorhombic structure (a-uranium). We have found that the surface does indeed support a magnetic moment. The results of the calculations for a monolayer and films with up to seven layers prove that the ferromagnetic phase is energetically favored over the paramagnetic phase. The calculated total magnetic moment per atom on the uranium monolayer is $2.01\mu_B$ and $1.75\mu_B$ in GGA and LSDA, respectively. The predicted total magnetic moment per atom on the surface of uranium film is $0.65\mu_B$ and it is stable upon the change in the slab thickness.

We believe that the surface magnetism in uranium can be observed experimentally. Given the size of our computed magnetic moments, these should be readily detectable.

Fascinating actinide materials - Recent electronic structure investigations

P.M. Oppeneer

Leibniz-Institute of Solid State and Materials Research, P.O. Box 270016, D-01171, Dresden, Germany

The electronic structure and electronic properties of several fascinating actinide compounds are investigated computationally. The symmetry of the order parameter of the heavy fermion super-conductor UPd2Al3 is studied by selfconsistently solving the gap

equation. Physically motivated pairing potentials are adopted, that are either due to small q-phonon processes, or to spin-fluctuations. The same unconventional d-wave order parameter is obtained with both types of pairing potentials. Electronic structure calculations for the new, medium-high TC superconductor PuCoGa5 show that the lattice constants are well-given assuming delocalized 5 f's. The electronic states at the Fermi energy are dominated by the Pu 5 f's. The superconductivity emerges thus out of the pairing of Pu 5f electrons.

Localized states and valencies in Rare Earth's and Transition Metal Oxides

W. Temmerman[1], Z. Szotek[1], A. Svane[2], L. Petit[2], P. Strange[3], H. Winter[4], R. Tyer[1], G. Banach[1], G. Gehring[5] and M. Stocks[6]

[1] Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.
[2] Institute of Physics and Astronomy, Aarhus University, Aarhus, Denmark
[3] Physics Department, Keele University, Keele, U.K.
[4] INFP, Forschungszentrum Karlsruhe, Germany
[5] Physics Department, University of Sheffield, Sheffield, U.K.
[6] Metals and Ceramics Division, Oak Ridge National Laboratory, TN, USA

The self-interaction corrected local-spin-density (SIC-LSD) method is discussed with respect to determining if an electron state forms part of the valence band complex or is localized. It will be shown that this leads to an useful definition of valency and this will be compared with the standard ionic valency definition. The examples used for the argumentation concern: (1) rare earth's and their compounds, (2) metal-insulator transition in YBa2Cu3O7-x as a function of O concentration, (3) orbital order in LaMnO3, (4) charge order in Fe3O4.

Properties of actinide elements

O. Eriksson

Department of Physics, Theoretical Magnetism Group, Box 530, SE-751 21, Uppsala, Sweden

The electronic structure of the actinides is reviewed with special emphasis on how it influences the materials properties. Special emphasis will be put on the different phases of Pu, where several of the recent suggested models to explain the unique phase diagram will be reviewed.

List of Participants

Pascal Boulet, ITU Karlsruhe, Germany (boulet@itu.fzk.de)

M.S.S. Brooks, ITU Karlsruhe, Germany (brooks@itu.fzk.de)

Roberto Caciuffo, Università di Ancona, Italy (rgc@unian.it)

Mamo Colarieti-Tosti, ITU Karlsruhe, Germany (m.ct@itu.fzk.de)

Eric Colineau, ITU Karlsruhe, Germany (colineau@itu.fzk.de)

Michel Eckle, ITU Karlsruhe, Germany (michel.eckle@itu.fzk.de)

Rachel Eloirdi, ITU Karlsruhe, Germany (rachel.eloirdi@itu.fzk.de)

Olle Eriksson, University of Uppsala, Sweden (olle.eriksson@fysik.uu.se)

Thomas Gouder, ITU Karlsruhe, Germany (gouder@itu.fzk.de)

Jean-Christophe Griveau, ITU Karlsruhe, Germany (griveau@itu.fzk.de)

Tatiana Guidi, Università di Ancona, Italy (t.guidi@unian.it)

Ladislav Havela, Charles University, Prague, Czech Republic (havela@met.mff.cuni.cz)

Stephen Heathman, ITU Karlsruhe, Germany (heathman@itu.fzk.de)

Fuminori Honda, Charles University, Prague, Czech Republic (honda@mag.mff.cuni.cz)

Monique Idiri, ITU Karlsruhe, Germany (idiri@itu.fzk.de)

Börje Johansson, University of Uppsala, Sweden (borje.johansson@fysik.uu.se)

Frédéric Jutier, ITU Karlsruhe, Germany (frederic.jutier@itu.fzk.de)

Matej Komelj, Jovzef Stefan Institute, Ljubljana, Slovenia (matej.komelj@ijs.si)

Gabriel Kotliar, Rutgers University, U.S.A. (kotliar@physics.rutgers.edu)

Gerard H. Lander, ITU Karlsruhe, Germany (lander@ill.fr)

Peter Normile, ITU Karlsruhe, Germany (peter.normile@itu.fzk.de)

Peter Oppeneer, Institute of Solid State & Materials Research, Dresden, Germany (p.m.oppeneer@ifw-dresden.de)

José A. Paixão, University of Coimbra, Portugal (jap@pollux.fis.uc.pt)

Karel Proke, Hahn-Meitner-Institute, Berlin, Germany (prokes@hmi.de)

Vítor Rodrigues, University of Coimbra, Portugal (vhugo@pollux.fis.uc.pt)

Axel Svane, Aarhus University, Denmark (svane@phys.au.dk)

Walter Temmerman, Daresbury Laboratory, Warrington, U.K. (w.m.temmerman@dl.ac.uk)

Gerrit van der Laan, Daresbury Laboratory, Warrington, U.K. (g.van_der_laan@dl.ac.uk)

Hilbert von Löhneysen, Physikalisches Institut, Universität Karlsruhe und Forschungszentrum Karlsruhe, Institut für Festkörperphysik, Karlsruhe, Germany (h.vL@ifp.fzk.de)

Franck Wastin, ITU Karlsruhe, Germany (wastin@itu.fzk.de)

5 News from the RTN3 Network ("Exciting")

"Optical Properties of Solids" (Exciting)

5.1 RTN3 Workshop Announcements

5.1.1 EU RTN "EXC!TiNG" Summer School on "DFT beyond the ground state"

June 22-30, 2003, Riksgränsen, Sweden

This is to inform you that the EU RTN "EXC!TiNG" Summer School on "DFT beyond the ground state" will take place in Riksgränsen, Sweden, June 22-30, 2003. There will be given a number of lectures, as well as a number of contributed papers at the school. Target audience for the lectures is mainly Ph.D. students and Post-Docs.

Speakers include: Rajeev Ahuja (Uppsala), Claudia Ambrosch-Draxl (Graz), Torsten Andersen (Uppsala), Ulf von Barth (Lund), Silvana Botti (Ecole Polytechnique), Andrea Damascelli (UBC, Vancouver), Olle Eriksson (Uppsala), Xavier Gonze (Louvain), Eberhard K. U. Gross (FU Berlin), Björgvin Hjörvarsson (Uppsala), Julius Hohlfeld (Seagate), Bengt Holm (Lund), Wolfgang Hübner (Kaiserslautern), Börje Johansson (Uppsala), Bert Koopmans (Eindhoven), Wolfgang Kuch (MPI-Halle/Bessy), Jan Kunes (UC Davis), Kjeld Pedersen (Aalborg), Alice Ruini (Modena), Sangeeta Sharma (Graz), Adolfo G. Eguiluz (UT Knoxville), Brian Vohnsen (Murcia).

Programme, as well as additional information is available at the schools web-page:

  `http://www.fysik4.fysik.uu.se/~thor/school.html` .

Lecture notes and contributed papers will appear in Proceedings.

Registration deadline was May 16, 2003, but we still have a few (about 5) places left at the subsidized price of 7000 SEK per person in single rooms and 6000 SEK per person in double rooms (excl. VAT - institutions with VAT number do not have to pay VAT).

There are also still possibilities to contribute a Poster and a paper for the proceedings.

Torsten Andersen

(For the Organizing Committee)

6 News from the TMR2 Network

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

6.1 Final Report on the TMR2 Network Activity

Coordinator:

Axel Svane

Department of Physics and Astronomy

University of Århus,

DK-8000 Århus, Denmark

Period covered by this report: 60 months; 01-03-1998 - 28-02-2003

Network home page: `http://www.ifa.au.dk/\~{ }svane/tmr-psik.htm`

SUMMARY

This Network has been operating for 60 months. 20 young researchers have been financed under the contract for a total of 371 PostDoc man-months, exceeding the contractual number, 264, by 40 %. All young researchers have continued after their Network association with employments in academia or industry. 61 joint publications and 71 publications involving Network PostDocs have been published, and several are in the pipeline as the collaborations established with this Network continue into the future. All major milestones of the scientific Work Program have been met, and a good deal of additional research results have been accomplished. A total of 27 workshops, mini-workshops and other scientific/coordination meetings have been organised and partly or fully supported by the Network grants.

The main effort of the Network has been devoted to the advancement of the *ab-initio* quantum mechanical modelling of solid state systems. Significant progress has been made in developing the computer software into general multi-purpose packages. These developments have been done in a suite of the most widespread electronic structure codes (LMTO, VASP, FLAPW). All codes have been enhanced with the capabilities of describing non-collinear magnetism, as well as spin-orbit interactions and the LDA+U option. Optics and magneto-optics properties are implemented in the FLAPW code, as well as molecular dynamics, transport properties and electron-phonon interactions. The VASP code includes

spindynamics and incommensurate spin-helical structures. To this comes the adaptation of all codes to state-of-the-art hardware, most notably the efficient parallellization of the computations.

A significant part of the Network efforts have been devoted to the development, testing and implementation of improved descriptions of correlated systems, like f-electron materials and superconductors, as well as of excitations in solids.

The methodology has been applied to a large number of important examples, the published results of which serve as the ultimate validation of the quality of the developments. In doing so, examples from many areas of materials science have been selected to demonstrate the wide applicablity of the present density-functional based methodology. In particular, several industrially relevant systems have been investigated.

PART A - RESEARCH RESULTS

A.1 Scientific Highlights

Complex magnetic structures

With the developments of the present Network, the completely *ab-initio* investigation of non-collinear magnetic systems has been facilitated, and a vast number of problems regarding the complex magnetic structures found in Nature lay open for in-depth research. During Network operation, non-collinear magnetism has been successfully investigated - and Network publications completed - for several 3d metal systems: $\alpha-$Mn and $\beta-$Mn, ordered intermetallic γ-Fe-Mn compounds and disordered solid solutions, incommensurable spin-helices in $\gamma-$Fe, several 3d films, $La(Ca_xSr_{1-x})MnO_3$ and YMn_2 and Y-Mn-Sn systems. Recently, the α phase of Pu was also attacked with this methodology.

Catalysis: Interaction of O_2 and H_2O with a Fe_2O_3 surface.

Insight into the mechanisms of catalysis on the atomic level is a major goal of materials science today. The (0001) surface of Fe_2O_3 (hematite) has been studied including antiferromagnetic ordering. An extensive investigation of the thermodynamic stability of various oxygen coverage and surface structures was carried out, including energetics of chemisorption and dissociation of molecular oxygen on that surface. Using a thermodynamic model to represent the interaction between the $Fe_2O_3(0001)$ surface and molecular oxygen in the gas phase above the surface at various temperatures and pressures, a series of stable and metastable surface structures were established. A particular structure contains an Fe atom at the surface with an on-top O atom, which can be released at elevated temperatures. It is remarkable that this arrangement of the atoms is the most stable structure at the temperature and pressure conditions, which apply for industrial iron oxide catalysts in the selective oxidation of ethylbenzene to styrene. For water molecules interacting with the $Fe_2O_3(0001)$ surface, a most remarkable finding is the coexistence of three different structures at 800 K at an O partial pressure of 0.2 bar. The implications are that this surface can accept and release H and O atoms, as is needed in a catalytic process such

as the abstraction of H from an adsorbed ethylbenzene molecule and subsequent regeneration of the surface by release of H_2O and dissociation of O_2. These new results have significant bearings on our understanding of the catalytic activity of iron oxides as well as the interaction of oxygen and water in the context of corrosion.

First-principles calculation of the properties of the Nb/α-alumina interface.

The equilibrium structures of the $Al_2O_3(0001)$ surface and the $Nb(111)/\alpha$-$Al_2O_3(0001)$ interface have been calculated, both in vacuum and with varying partial oxygen pressure, P_{O_2}. The largely ionic nature of the interface bonding has been analysed in terms of bond orders and Mulliken populations. A formalism has been developed, useful for first-principles calculations, which relates the free energy of an oxide/metal interface to the free energies of surfaces and the work of separation of the interface. From total energy calculations for the $Nb(111)/\alpha$-$Al_2O_3(0001)$ interface, and for free Nb and $Al_2O_3(0001)$ surfaces, the work of separation is numerically determined, which is independent of P_{O_2}. In the next step surface energies, interfacial energies and the equilibrium work of adhesion as a function of P_{O_2} are determined. In the case of Nb/alumina the Al-terminated interface has been identified as the thermodynamically more stable, although mechanically weaker, over most of the range of oxygen pressures considered. However, near the upper range of oxygen pressure (at which the oxide NbO begins to form) the energy difference is too small to be resolved by our present methods. The *ab-initio* calculation of surface phonons of alumina have been completed, and their implications on termodynamic properties of alumina surfaces investigated.

The volatility of the f-shell: Simple rules for determining the valencies of f-electron systems.

The self-interaction corrected (SIC) local-spin-density (LSD) approximation allows an interpolation between a completely localized f-shell and fully delocaliced f band electrons. The f-manifold is divided into localized and delocalized electrons, and the optimum way to do this split is determined fully *ab-initio* by the total energy. The SIC-LSD computer code has been extended to treat all relativistic effects including spin-orbit coupling. Applications of the scheme to all elemental $4f$ and $5f$ metals and to a large number of f-electron compounds have revealed a simple picture of the effective valency in f-electron systems. The formalism describes correctly the valency changes observed in the series of the $4f$ and $5f$ metals. Similarly, the trends of valency stability of the $4f$ sulphides are reproduced and follow the same universal picture as the $4f$ elements. A quantitative description of valency changes as a function of pressure is likewise obtained for a series of rare earth compounds, and this has also led to the identification of some yet unobserved high-pressure phase transitions. In AB compounds, with A an actinide element and B an element from groups V or VI in the Periodic Table, the systematic shift in valency from A=U to A=Cm is investigated. The role of the U f-electrons in the UM_3 (M=Rh, Pd, Pt, Au) has been described, with in particular UPt_3 showing intriguing properties, halfway between the localized and delocalized pictures.

Improved description of excited states

The ab-initio description of excited states in insulating materials is of the utmost importance for the quantitative understanding of the properties of many electronic devices. Results for excitation energies and ionization potentials based upon standard schemes such as LDA or GGA are often not sufficiently accurate, for which reason the screened-exchange LDA functional (SX-LDA) has been implemented in a planewave pseudopotential code with parallel and ultrasoft pseudopotential capabilities. The SX-LDA is formulated with a well defined total energy in a perturbative fashion, and full use is made of that capacity to perform molecular dynamics calculations. Fully self-consistent calculations are performed, yielding meaningful ionic forces. In fact, the SX-LDA reduces the self-interaction implicit in LDA, which has a major effect in the ionic forces. In particular, the vacancy defects in pure Germanium have been studied. Ge is predicted to be a metal by conventional LDA calculations, which makes it difficult to assess the deep levels induced by these defects.

The excitations problem has also been approached by the time-dependent(TD) density functional theory formalism. Excellent results have been obtained for finite systems such as atoms, molecules and clusters using LDA or GGA exchange-correlation kernels, as well as for metals. This has not been the case for insulators. The key point is that these functionals miss the long range behavior of the exchange-correlation kernel in semiconductors, and the corrections have been shown to vanish in the thermodynamic limit. It has been clarified that the exchange-correlation functional needs a dependance on the polarization, which determines the long-range behavior of the kernel and thus the response for extended band to band excitations as compared to local approximations based on the electron gas. The exchange-correlation dependence on the polarization is so far unknown. The standard TD-LDA and TD-LSD has been implemented and tests have been performed for localized excitations in the diamond vacancy, in particular the ND1 line observed for the negatively charged vacancy.

The ab-initio understanding of the phenomenon of superconductivity

The construction of first-principles functionals for the exchange and correlation energy in the superconducting state has been accomplished. A universal LDA-type functional describing the purely electronic correlations in superconductors has been developed. The functional is constructed from the exchange-correlation free-energy density, f_{xc}^{hom}, of a homogeneous electron gas, exposed to an external translationally invariant pairing field. The quantity f_{xc}^{hom}, which is a function of the density and of the induced order parameter, is calculated with many-body perturbation theory by an RPA-type resummation of all normal and anomalous bubble diagrams. In a second step, functionals describing the electron-phonon coupling have been derived. By putting both functionals together and solving the resulting gap equation, the critical temperatures of simple metals have been succesfully calculated, as well as the the full k-dependance of the gap function. The agreement of the calculated T_c's and the experimental numbers, being typically within a few percent, is very encouraging.

The quasiparticle spectra of the high T_c superconducting compound $YBa_2Cu_3O_{7-\delta}$ has been calculated from first principles. The calculations are based on the eight-band model developed by Andersen and coworkers to describe the energy bands associated with the CuO_2 bilayers near the Fermi energy, combined with a phenomenological description of the electron-electron attraction. The parameters of the eight-band model were determined by first-principles LDA calculations plus one coupling constant chosen to reproduce the experimentally observed T_c of 92 K at optimal doping. Thus, in the above well-defined sense, the theory is free of adjustable parameters. The new quantities calculated were the two components of the penetration depth tensors λ_a and λ_b, as functions of the temperature T and doping. Recently, this has been extended into studies of the ferromagnetic superconductor $RuSr_2GdCu_2O_8$.

Relativistic effects in superconductors have been studied, including the dichroism in the electromagnetic response of superconducting-normalconducting (SN) multilayers, produced by the anomalous spin-orbit coupling. The structure of this spin-orbit term is similar to the ordinary spin-orbit coupling, but it involves the pairing field in place of the electrostatic potential. It is large whenever the gradient of the pairing potenial is large, which in particular happens in SN multilayers.

Fully relativistic LAPW codes with molecular dynamics, phonons and optics.

Magnetic anisotropy and magneto-optical properties are now accessible with the extensions implemented into the LAPW computer code. In addition, static planar electric fields have been included in the codes, and this has been used to investigate electron densities and internal strains due to the electric field in GaAs and to interprete synchrotron diffraction measurements. The effect of an applied electric field on the magneto-crystalline anisotropy has been studied and a patent obtained, as this has potentially a large impact on the performance of magnetic recording devices. The electron-phonon coupling constants in metals have been calculated by two different procedures: The required quantities have been obtained from (a) two self-consistent calculations, or (b) by use of the linear response method. The results of both methods excellently agree for all test substances and phonon modes. The method is applied to study q-dependent electron-phonon coupling constants in superconducting materials.

The Psi-k2000 Conference

The Psi-k2000 Conference was held in Schwäbisch Gmünd in August 2000, and marks the organisatorial culmination of our Network. About 420 people participated in this event. Within the field of electronic structure calculations of materials the Psi-k2000 conference is unmatched worldwide, as also evidenced by the large number of colleagues from America and Japan who participated at this conference. The conference was organised into 19 symposia, of which there were symposia specializing in each of the subprojects of the present Network, with the exception of 'LAPW', which was covered in the more general 'Band Structure Methods' symposium, and the 'Training and Dissemination' subproject, which does not include research but on the other hand was the main provider of the logis-

tics of the meeting. The meeting had 4 plenary speakers, 103 invited speakers including 9 from industry, and 111 contributed talks, and 154 posters. All Network post-docs employed at the time presented research contributions at the meeting, which also hosted the Midterm Review meeting.

PART B - COMPARISON WITH THE PROJECT PROGRAMME

B.1 Research Objectives and Methodological Approach

The Network research comprises atomic-scale computer simulation methodology to understand complex properties and processes in solids and at solid surfaces of a type relevant to industry and basic science. The aim has been to develop the methodology of ab-initio computer simulations and to demonstrate its capabilitites to problems of interest to industry. These objectives have successfully been accomplished as outlined in Section **A.1**.

The methodology employed is that of large-scale 'ab-initio' quantum mechanical computer calculations of properties and processes at the scale of the individual atoms in solids and at solid surfaces. The research is based on the density functional formulation of quantum mechanics, which is implemented in a suite of computer codes, each covering one particular aspect of the problem at hand. The Network project has been divided into eight flagship subprojects, each spear-headed by one of the Network partners.

The Table below illustrates how the Network partners were involved in the subprojects.

	1 Surfac.	2 f-elect.	3 Interf.	4 Magn.	5 LAPW	6 Excit.'s	7 Supercond.	8 Training
MSI	x		x		x			x
ISMANS	x		x	x				x
AARHUS		x		x	x	x	x	x
QUB	x		x					x
WIEN	x	x		x	x			x
FZJ	x	x	x	x	x			x
HUT				x	x	x		x
UWUERZ		x				x	x	x
CCLRC		x	x			x	x	x

Table 1: Involvement of the Network partners in the Subprojects.

B.2 Comparison with Workplan

In the following the detailed workplan (as revised October 2001) for the eight subprojects is compared to the actual research accomplished in the Network.

- Subproject 1: **Surfaces**
  The **Surfaces** subproject was inactive for 2 1/2 years of the Network operation due

to move of the scientist-in-charge at partner MSI. Subsequently, the MSI partner withdrew from the Network, and ISMANS entered, taking over the responsiblities of MSI. In particular, ISMANS took over the scientific leadership of the **Surfaces** subproject, aiming to demonstrate the capabilities of advanced total energy electronic structure methods in the context of molecular processes on proto-typical catalytic oxide surfaces. Due to the considerable delays, efforts were focused on the Fe_2O_3 surface.

1. **Task 1A**: Calculation of structural and electronic properties of clean Fe_3O_4 surface without and with O-vacancies. This task has not been accomplished, as explained above.
2. **Task 1B**: Calculation of structural and electronic properties of clean Fe_2O_3 surface without O-vacancies: **DONE**. Investigations of oxygen vacancies and dissociation of H_2 and O_2 molecules on this surface: **DONE**.
3. **Task 1C**: Calculation of the reaction pathway of dehydrogenation of ethylbenzene to styrene on the Fe_2O_3 surface. This has not been accomplished, but is being pursued after the Network came to an end.
4. **Task 1D**: Calculation of the interface between water and the Fe_2O_3 surface: **DONE**.

- Subproject 2: **f-electrons**
  The AARHUS partner is the leader of this subproject, which developed the methodology of the self-interaction corrected density functional approach, and applied it to f-electron materials.

  1. **Task 2A**: Development and implementation of the relativistic and spin-polarised self-interaction corrected local spin density: **DONE**
  2. **Task 2B**: Application to Uranium and other 5f compounds: **DONE**
  3. **Task 2C**: Implementation of the full-potential total energy: **INCOMPLETE** This task has partly been overtaken by events. In particular, it became more urgent to speed up the SIC computer code to tackle more complicated systems. First full-potential aspects were included in published work on high-T_c superconductors.
  4. **Task 2D**: Excitations: **INCOMPLETE**. A self-interaction corrected theory for calculating crystal field splittings has been developed by the external team member in Uppsala. Excitations may be calculated as total-energy differences, but a general-purpose code has not been developed, partly due to the considerable difficulties encountered by the **Excitations** subproject.

- Subproject 3: **Interfaces**
  This subproject has demonstrated the application of the methodology to oxide surfaces and interfaces.

  1. **Task 3A**: Metal on Al_2O_3 aluminium oxide interface structure and energy by ab initio calculation: **DONE**. Experimental work on metal-spinel interfaces

in Stuttgart established the relative translation of two crystals with picometre precision, which was accounted for in the DFT calculations. The equilibrium stoichiometry of surfaces and interfaces was also studied theoretically at QUB as a function of temperature and oxygen partial pressure. Alumina however has presented unexpected difficulties which were the impetus for new theoretical development, not on the original workplan. Following careful zero temperature calculations, discrepancies of order 20pm between calculated and experimental positions of oxygen atoms on the alumina(0001) surface became apparent. The reason was suspected to be anharmonicity, hence over the last year work on the lattice dynamics of alumina and its (0001) surface was completed, including a study of its effect on surface free energy. As a result, anharmonicity appears to be a very unlikely candidate to explain the experiments, and DFT approximations (LDA and GGA) must also be questioned in this system.

2. **Task 3B**: Development of ab initio benchmark tests for approximate methods: tight binding (TB), Harris functional, and Discrete Classical Model (DCM): all for Nb, Al, Fe on Al_2O_3. **INCOMPLETE**. Despite considerable efforts a satisfactory functional has not been found at time of Network completion.

3. **Task 3C**: Application of TB method to diffusion of metal atoms (Nb, Al, Fe) on Al_2O_3 and mechanism of their crystal growth on the oxide. Try application of DMC and TB to dynamic calculations. **INCOMPLETE**, for reasons given under **Task 3B**.

4. **Task 3D**: metal/$BaTiO_3$ and metal/$SrTiO_3$ interfaces. **DONE**

- Subproject 4: **Magnetism**
  This subproject involves the development of the methodology to include non-collinear magnetic moments in all major European codes with applications.

  1. **Task 4A**: Implementation of non-collinear magnetic moment capability to enhance all major European codes LMTO, ASW, LAPW, TB-LMTO, CPA-DLM. Continuously varying quantization axis, spin-orbit and orbital effects. **DONE**

  2. **Task 4B**: Tools for spin dynamics **DONE**

  3. **Task 4C**: Application of non-collinearity to intermetallic compounds including incommensurate structures. Spin-glass and aspero magnetism in disordered and amorphous alloys and compounds. **DONE** Several applications have been mentioned in Section **A.1**.

  4. **Task 4D**: 'Giant' and 'colossal' magnetoresistive materials (GMR and CMR). **DONE**

  5. **Task 4E**: Canted spin structures and magnetic anisotropy in thin films and exchange-coupled superlattices. **DONE**

- Subproject 5: **LAPW**
  This subproject has extended the LAPW methodology into the realm of ab-initio molecular dynamics for magnetic materials with applications to surface reactions.

  1. **Task 5A**: Development of LAPW codes for ab initio molecular dynamics calculations on parallel computers: **DONE**

2. **Task 5B**: Development of a spinpolarised, relativistic (including spin-orbit interaction) LAPW code applicable to non-collinear magnetic systems: **DONE** This includes the capabilities of non-collinear magnetism, local-orbitals, and LDA+U. In addition, the LAPW program suite now includes codes to compute the optical and magneto-optical properties of materials, and electron-phonon coupling.

3. **Task 5C**: Application to dynamics of catalytic reactions at transition-metal surfaces: **DONE**

4. **Task 5D**: Application to structure, magnetism and growth of low-dimensional magnetic systems: **DONE**

- Subproject 6: **Excitations**
  This subproject involves the development and implemetation of the methodology to electron excitations and optical properties in solids. This subproject has involved tests of several schemes proposed for the excitation problem, most emphasis put on the screened-exchange LDA functional and time-dependent LDA.

  1. **Task 6A**: Implementing the time-dependant LDA procedure for calculating excitation energies in a plane wave and pseudopotential code. Tests on atoms and the silicon band gap. **DONE**. Refinements of the theory are still needed, as the applications to extended systems proved the existing formalism insufficient. A real-space implementation has been developed. Applications to fullerene structures and semiconductor clusters have been completed.

  2. **Task 6B**: Application to wide-gap semiconductors of interest to industry, particularly luminescence spectra of phosphides and nitrides (GaP, GaN, AlN) pure and with dopants. **DONE**. Extensive applications of the screened-exchange LDA functional has been completed on semiconductor systems.

  3. **Task 6C**: Developing a code for laser applications, particularly laser pulses and non-linear response. **INCOMPLETE** due to the problems mentioned under **Task 6A**. As a replacement, the study of quantum dots with the finite-size approach of **Task 6A** was completed. This includes the interaction between a superconductor and a quantum dot.

  4. **Task 6D**: Application to chemical precursor states of atoms adsorbed at surfaces, including resonant charge transfer with ionisation of atoms and neutralisation of ions. **INCOMPLETE** due to the problems mentioned under **Task 6A**.

- Subproject 7: **Superconductivity**
  This subproject has extended the methodology into the realm of ab initio calculations of superconducting properties.

  1. **Task 7A**: Solving the Bogoliubov-de Gennes equations for the low energy LSD Hamiltonians. Study the materials-specific aspects and the role of doping. Calculate specific heat, spin-lattice relaxation rates and penetration depths. **DONE.** This has been carried through in both $YBa_2Cu_3O_7$ and $RuSr_2GdCu_2O_8$ high T_c superconductors.

2. **Task 7B**: Implement an approximate scheme which decouples the BdG equations into a normal Kohn-Sham equation and a gap equation which contains xc contributions in addition to the BCS mean-field terms. Test in this scheme first-principles LDA-type xc potentials for superconductors: **DONE**. The gap equation has now been solved in both the linear and non-linear version, and critical temperatures have been successfully calculated.

3. **Task 7C**: A relativistic theory of superconductivity has been developed to study dichroism in superconductors. **DONE** A review article on relativistic effects in superconductors has been published. The dichroic response of normal-superconducting-normal metal multilayers has been investigated.

- Subproject 8: **Training and Dissemination**
  This subproject is dedicated to the coordination of the training and dissemination of the methodology.

  1. **Task 8A**: Dissemination: Publication of Psi-k Newsletter every 2 months. Running of the Majordomo e-mail list to distribute news fast. Keeping the WWW-page information up-to-date: **DONE**. 30 newsletters have been published during the Network operation, containing all news and reports on Network activities.

  2. **Task 8B**: Training: Provide coordination to the scientific and organisatorial meetings of the Network: **DONE**. In total this Network has organised or co-organised 27 meetings, including 1 large conference, 10 research workshops, 3 mini-workshops, 5 tutorials, and 8 Network management board meetings. See Section **B.3**.

  3. **Task 8C**: Organise a Conference for all research groups in the Network (and relevant people outside), devoted to the subject of electronic structure calculation of materials, with special theme of reaching out to industry. **DONE**. This was the Psi-k2000 conference.

B.3 Principal Networking Activities

This Network has hired in total 20 young researchers for altogether 371 PostDoc man-months of research activities. The PostDocs are listed in Table 2. The total research efforts of each Network partner are listed in Table 3.

The Network has organised or co-organised a total of 27 meetings:

1. Industry Workshop: *Electronic Structure Calculations for Industry and Basic Sciences*, Wien, June 1998. (60 attendees, 8 Network partners represented)

2. Network Management Board meeting, Wien, June 1998, (10,8)

3. Network Management Board meeting, Paris, October 1998, (10,8)

Name	Nationality	Age	Start Date	months	partner
José Luis De Los Mozos Liz	**ES**	32	1/5/98	28	HUT
Peter Gravil	**GB**	30	1/6/98	9	MSI
Gustav Bihlmayer	**AT**	32	1/9/98	24	FZJ
Lars Fast	**SE**	33	1/10/98	36	UWUERZ
David Hobbs	**IE**	28	15/10/98	24	WIEN
Sean Clarke	**GB**	25	1/11/98	24	FZJ
Barbara Montanari	**IT**	29	1/2/99	24	QUB
Arnaud Marmier	**FR**	28	15/8/99	36	QUB
Leon Petit	**LU**	35	1/9/99	36	AARHUS
Jason James Hogan-O'Neill	**GB**	26	15/1/00	18	HUT
Georg Madsen	**DK**	28	1/2/00	12	FZJ
Martijn Marsman	**NL**	29	1/3/01	24	WIEN
Nektarios Lathiotakis	**GR**	32	1/9/00	29	UWUERZ
Manuel Perez Jigato	**ES**	35	1/8/01	19	HUT
Wolfgang Bergermayer	**AT**	30	1/2/02	12	ISMANS
Hannes Schweiger	**AT**	31	1/5/02	10	ISMANS
Miguel Marques	**PT**	27	15/5/02	2	UWUERZ
Andrea Floris	**IT**	29	15/5/02	2	UWUERZ
Markus Dane	**DE**	23	14/7/02	1	CCLRC
Diemo Koedderitzsch	**DE**	28	7/7/02	1	CCLRC

Table 2: List of Young Researchers. First 18 are post-doc's, last two pre-doc's.

4. LAPW mini-Workshop, Jülich, November 1998, (22,3)

5. Superconductivity workshop: *The V'th Bristol Workshop on the Boguliubov-de Gennes equations*, Bristol, November 1998, (35,2)

6. Topical Workshop: *Materials Under Pressure: From Ices to Metals*, Daresbury, December 1998, (30,3)

7. LAPW hands-on workshop, Wien, April 99, (40,4)

8. Workshop: *Catalysis from first-principles*, Magleås (Denmark), May 1999, (50,4)

9. Topical Workshop: *International Workshop on Orbital and Spin Magnetism of the Actinides*, Daresbury, June, 1999, (30,3)

10. Carr-Parrinello hands-on workshop, Trieste, August 99, (80,6)

11. Network Management Board meeting, Paris, October 1999, (10,7)

12. Psi-k2000 Conference Coordination meeting (Program Committee), Paris, December 1999, (20,7)

Participant	Network post-doc		other researchers	
	28 months	60 months	28 months	60 months
AARHUS	10	36	32	96
MSI	9	9	7	7
ISMANS	0	22	0	7
QUB	27.5	60	69	189
WIEN	20.5	48	43	122
FZJ	47	60	58	138
HUT	31.5	65	30	105
UWUERZ	21	69	35	95
CCLRC	0	2	55	170
Total .	166.5	371	329	929

Table 3: Total research effort in man months for post-docs financed by the Network and for other researchers (for 28 months (midterm), and for 60 months.)

13. Superconductivity workshop: *The VI'th Bristol Workshop on the Boguliubov-de Gennes equations*, Bristol, April 2000, (44,2)

14. FLAPW hands-on Workshop *Full-Potential LAPW Calculations with the WIEN97 Code*, Wien, April 2000, (64,4)

15. SIC mini-Workshop: *Electronic Structure and Magnetism in Strongly Correlated Systems*, Daresbury, May 2000, (11,2)

16. Psi-k2000 Conference, Schwäbisch Gmünd, August, 2000, (420,9)

17. Midterm Review meeting, Schwäbisch Gmünd, August, 2000, (19,8)

18. Network Management Board meeting, Schwäbisch Gmünd, August, 2000, (8,8)

19. Discussion meeting: *Catalysis from first principles*, Lyon, July 2000, (46,4)

20. Workshop, *Non-collinear magnetism*, Wien, March 2001, (35,4)

21. Workshop, *The physics of f-electron systems*, Daresbury, April 2001, (37, 5)

22. FLAPW hands-on Workshop *Full-Potential APW+lo Calculations with the new WIEN2k Code*, Wien, September 2001, (40,4)

23. Network Management Board meeting, Paris, October, 2001, (7,7)

24. Workshop, *Catalysis from first principles*, Wien, February 2002, (55,5)

25. Network Management Board meeting, Paris, October, 2002, (8,7)

26. VASP hands-on Workshop, Wien, February 2003, (40,3)

27. LAPW mini-Workshop, Jülich, February 2003, (22,3)

B.4 Interactions to Industry

The MSI partner was the only industrial partner in this Network. After the MSI scientist-in-charge, Dr. E. Wimmer, moved, this partner decided to withdraw from the Network. Instead the new affiliation of Dr. Wimmer, partner ISMANS, entered the Network. ISMANS is an educational organisation, however with many contacts to industry, and Dr. Wimmer continued to guaranty the industrial perspective of the Network operation. While in the Network, MSI, together with partner TU-WIEN were the main organizers of the 'Industry Workshop' in June, 1998, which invited a mixed selection of academic and industrial researchers for exchange of science. This Workshop has developed into an annual event in the area of Catalysis, still with partner TU-WIEN (now UNI-WIEN) as one of the main organizers. At the Psi-k2000 conference 9 industrial speakers gave lectures of their research. During the Network operation, Industry has shown increasing interest in our simulation methodology. Several of the computer packages developed by the partners of the Network are now disseminated into Industrial groups, where they are used as a natural part of the R&D efforts.

B.5 Assessment: Benefits from working together at a community level

The Network was given collaborative opportunities not available from any other funding agency. All the Network subprojects benefited from substantial collaborations between the partners. Most important was the access to travel funds for regular scientific meetings, where in particular the young researchers may discuss their science in an international forum and aquaint with other people sharing their interests, they develop their personal Networks and maybe initiate collaborations. The meetings organised by the Network took advantage of this, and several secondments of young and senior researchers were financed, albeit primarily for shorter time periods than one month. The informal exchange of information regarding the implementation of various features in either of the software packages maintained by the partners is of considerable value. The newsletter has been invaluable in being the prime place for research groups to post their developments, either in the abstracts section or as one of the bi-monthly scientific highlights. All Network partners have contributed to the hightlights section of the newsletter during the 5 years of operation.

The Network has provided their young researchers with the opportunity to acquire significant scientific skills through a process, which effectively can only be accomplished by working within a European-wide Network. The field of computational materials science has become extremely complex and the training process is long and tedious. However, from the contact with industry it is obvious that the European Union needs, more than ever, highly trained and motivated scientists and engineers, who can translate the leading scientific role of Europe in this field into industrial innivation and competitiveness. To this end, a European-wide Network among colleagues is an invaluable asset. The experience gained from the present project clearly fulfilled the vision of the European Commission, when it established this programme for the training and mobility of researchers.

B.6 Assessment: Network contribution to the training and mobility of researchers

Overall we believe that we have provided a thorough training of the young researchers in the Network. The fact that all of them have continued directly from their Network employment into either other Post-Doc stipends, academic tenure track positions, or industrial employments, speaks for itself. The access to many meetings helps to integrate the young researchers into the community, and in particular the Psi-k2000 conference, in addition to its primary goal of scientific information exchange, serves the secondary purpose of putting the narrow research area of the individual into the broad perspectives of the community. Several of the Network meetings focused directly on the tutorial purpose of dissemination of software codes developed in the Network, which benefited both Network Post-Docs and other European young researchers.

7 News from the ESF Psi-k Programme

"Towards Atomistic Materials Design (Psi-k)"

7.1 Call for Workshop Proposals for 2004

It is time to consider proposals for workshops, hands-on tutorials, etc. to be held in 2004 for (partial) funding by the ESF Psi-k Programme.

A proposal should be submitted by email (in the form of a single simple email letter WITHOUT ATTACHMENTS OR LATEX, just plain ASCII) to the Psi-k Programme secretary, Walter Temmermann, at

psik-coord@dl.ac.uk

by 15 August 2003 as absolutely final deadline. (Sorry the date is so early, due to Walter being busy with his conference and other travel.)

The proposal should include the following points (preferably numbered in this order).

1. Title and purpose of the workshop, with names and addresses (including email) of the organisers. See item (9) about an American co-organiser.

2. The scientific content and why a workshop would be useful at this time.

3. A tentative list of speakers whom it is hoped to have.

4. The number of participants it is planned to invite or attract, and their scientific involvement, e.g. as simulators, related experimentalists, code developers, etc., and young scientists in the subject.

5. Plans for a tutorial element and for attracting new researchers into the subject of the workshop. (If this is thought inappropriate for this workshop, please explain why.) The purpose of the ESF Psi-k Programme is to help everyone in our community to do good quality research, and in our expanding field this implies some outreach and tutorial activity.

6. Budget, expressed in Euro, and how much is being applied for from the ESF Psi-k Programme. In the past, this has been limited to about 9k Euro.

7. A statement about other organisations which will be applied to for co-sponsorship and additional funding, e.g. any EU RTN Network, CECAM, CCP-9 in the UK, etc..

8. Where it is hoped the workshop would be held.

9. Plans about inviting and financing any participants from America. See separate announcement directly after this one, about having an appropriate American co-organiser of the workshop.

Volker Heine
Chairman of ESF Psi-k Programme
vh200@phy.cam.ac.uk

7.2 Money for American Participation in European Workshops Connected with Psi-k, Cecam and Simu

There are various sources of money for bringing participants from USA to workshops in Europe. I have been given the following information.

The information is not very complete or precise, and it would be useful if people could give more detailed advice after they have successfully (or unsuccessfully) pursued any of these sources, and publish it in the Psi-k Newsletter under the heading "More info about money for American participants in workshops" so that it can be accessed easily.

1. If an American is a co-organiser of the workshop and has a National Science Foundation research grant, then (s)he can get an extra supplement to that grant by applying to the NSF grant manager, specifically to bring American participants to the workshop. I understand there is (also?) a special pot of money in NSF for international collaboration in materials science, but I do not know whether or not that is a separate channel through a separate programme manager.

2. Grantholders of Office of Naval Research grants can get them supplemented in the same way as in [1].

3. I am told that the NSF has special bilateral NSF International Programs with most European countries [but not with Europe or the EU collectively] which can support workshops, but there may(?) have to be approaches made from both ends. Website http://www.nsf.gov/home/int/

4. The US Department of Energy has an Office for Basic Energy Sciences, with a section on Materials Sciences and Engineering (with website) which has various projects running. If a workshop co-organiser is involved in one of those projects, then presumably the workshop is also relevant to the project and the co-organiser can apply for money in that way. The coordinator of two projects that look related to our types of workshop is John R. Rehr at University of Washington with email jjr@phys.washington.edu

5. The Materials Computation Center at the University of Illinois at Urbana/Champaign has a specific item in its budget for collaboration with Psi-k, Simu and Cecam. The Center includes people such as Richard Martin, Duane Johnson and David Ceperley who have participated actively in Europe in the past, but also covers some other people outside Urbana who take part in some projects of the Center. Any one of these as a co-organiser, or just personally as a participant coming to one of our workshops, can presumably ask for some of that money. Website http://www.mcc.uiuc.edu/

6. The Center for Molecular Modeling at University of Pennsylvania (director Michael L. Klein) also has a specific item in one of its grants for participation in Psi-k, Simu

and Cecam activities. The grant is a joint one including Roberto Car at Princeton, plus two or three other groups at other universities. A workshop co-organiser or participant actively associated with the grant or the Center can presumably ask for support from that grant.

7. There are various people doing our type of computer simulation at the Naval Research Laboratory in Washington DC, and in Department of Energy National Laboratories at Oak Ridge and Livermore. I do not know whether one of those paople, if a co-organiser of one of our workshops, would have access to Navy/DoE funds for American participants in the workshop.

Volker Heine
Chairman, ESF Psi-k Programme
vh200@phy.cam.ac.uk

7.3 ESF Psi-k Workshop Announcements

7.3.1 Workshop in San Sebastian

WORKSHOP ANNOUNCEMENT

AB INITIO ELECTRON-EXCITATIONS THEORY: TOWARDS SYSTEMS OF BIOLOGICAL INTEREST

21-24 September 2003, San Sebastian, Spain

http://dipc.ehu.es/arubio/dipc/bioex.html

Sponsored by the Donostia International Physics Center and the ESF/Psi-k Programme

The aim of this workshop is to assess the present status of theoretical approaches to the study of spectroscopic properties of real materials. In particular, the workshop will explore the capability of modern ab initio excited-state methods to describe complex systems with technological and biological interest. The different techniques employed in this context include many-body perturbation theory, time-dependent density-functional theory, configuration interaction as well as semi- empirical approaches. Therefore, this meeting is also intended to bring together scientists from different communities working on excited states and to find new solutions based on an exchange of experience. The workshop is part of an annual series organised by members of the European Research Training Network NANOPHASE.

Further details and instructions how to apply are available at

http://dipc.ehu.es/arubio/dipc/bioex.html

The deadline for applications is 20 July 2003.

The Organisers:

Pablo García-González (Universidad Autonóma de Madrid, Spain)
Maurizia Palummo (Università di Roma "Tor Vergata", Italy)
Olivia Pulci (Università di Roma "Tor Vergata", Italy)
Arno Schindlmayr (Forschungzentrum Jülich, Germany)
Nathalie Vast (Ecole Polytechnique, Palaiseau, France)

Position operator $\vec{r}$ in extended systems within DFT and HF.

Lyon, France, 29.09.-01.10.2003

Organizers

Name: Michael Springborg (contact organizer)

Affiliation: University of Saarland, Germany

Address: Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

Phone: +49 681 302 3856

Fax: +49 681 302 3857

e-mail: m.springborg@mx.uni-saarland.de

Name: Raffaele Resta

Affiliation: University of Trieste, Italy

Address: Dipartimento di Fisica Teorica, Strada Costiera 11,

I-34014 Trieste, Italy

Phone: +39-040-2240264, secr. 2240268

Fax: +39-040-224601

e-mail: resta@ts.infn.it

Scope

The quantum mechanical operator $\vec{r}$ (electronic position) is the key quantity for dealing with electric polarization in atomic, molecular, and solid-state physics. Whenever the electronic system is microscopic (atom, molecule, cluster...) the treatment of $\vec{r}$ is a trivial matter: its integral over the ground-state density provides by definition the dipole of the system, possibly in presence of a given external perturbation. For extended systems (linear polymers or 3d solids), instead, the treatment of the $\vec{r}$ operator has been a challenging issue over the years. Significant advances are occurring at this very time.

We are planning to bring together scientists from different communities (solids and molecules; chemists and physicists) in order to discuss different strategies for treating **r** theoretically for extended systems. A central issue is to exchange information between these communities and to develop improved approaches through new collaborations. Therefore, an informal character of the talks with much time for discussion is attempted. Two introductory overviews (by the organizers) will open the workshop followed by somewhat more

than 20 contributions.

Participation

Since the CECAM workshops typically are by invitation only, anyone interested in attending the workshop is asked to contact the organizers.

Further information

For further information, see:

http://www.mx.uni-saarland.de/fak8/springborg/workshop/homepage.html

7.3.3 XIII Workshop on Computational Materials Science

Second Announcement

13 - 18 September 2003

Calaserena Village, Geremeas (CA), Sardinia, Italy

Web page: http://www.dsf.unica.it/CMS2003

E-mail: workshop@dsf.unica.it

Organized by

The Physics Department, Università di Cagliari, and the Cagliari Research Unit of Istituto Nazionale per la Fisica della Materia

with the sponsorship of

European Science Foundation Program "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

and

Democritos Modeling Center for Research in Atomistic Simulation

under the patronage of UNESCO

An international workshop on computational techniques and applications to materials science

We would like to remind you that now is the time to REGISTER (deadline June 15) as a REGULAR PARTICIPANT. Since there are a few single rooms available, it is important to register as soon as possible.

FORMAT:

About 20 invited lectures plus TALK (12) and POSTER contributed session.

VENUE:

Calaserena Village at Geremeas (CA), an attractive sea resort on the south-eastern coast of Sardinia, providing comforts and an informal atmosphere.

CONTACT:

For scientific and logistic queries: workshop@dsf.unica.it

CONTRIBUTIONS:

Contributions in poster format are invited.

Deadline for abstract submission: July 15, 2003.

Contact F. Bernardini at +39 070 6754847, V. Fiorentini at +39 070 6754912 or P. Ruggerone at +39 070 6754869 or at workshop@dsf.unica.it for further details. LaTeX template for abstract can be downloaded from the homepage:

http://www.dsf.unica.it/CMS2003

INVITED SPEAKERS:

F.J. Himpsel (Madison, USA)
D. Marenduzzo (Oxford, UK)
M. Mareschal (Bruxelles, Belgium)
E. Molinari (Modena, Italy)
C. Molteni (Cambridge, UK)
M. Parrinello (Manno/Zuerich, Switzerland)
A. Pasquarello (Lausanne, Switzerland)
L. Reining (Paris, France)
E. Tadmor (Haifa, Israel)
J.P. Toennies (Goettingen, Germany)
E. Tosatti (Triest, Italy) (*)
D. Wolf (Duisburg, Germany)

(*) not yet confirmed

REGISTRATION:

The REGISTRATION form can be sent directly from the Workshop homepage (http://www.dsf.unica. The deadline is June 15, 2003.

The registration should be accompanied by payment receipt of the CONFERENCE FEE (by FAX: ++39-070-510171). The fee includes shuttle services (13/9 Cagliari Airport-Hotel, 18/9 Hotel-Cagliari Airport), full-board lodging at Calaserena Village from 13/9 to 18/9, coffee breaks, refreshments, and amounts to

Single room	Euro 667,50/person
Double room	Euro 550,00/person
Triple room	Euro 525,00/person
Quadruple room	Euro 525,00/person
Extra meal (if necessary)	Euro 23,25/person

Example: Single room + 1 extra meal = 690.75 (Total fee)

A very limited number of single rooms is available, we will process the Hotel Reservations on the first-come first-serve basis.

PAYMENT should be effected by bank money transfer, preferably by SWIFT, in EURO net of any bank charges, on the bank account No 22698 of Comitato Organizzatore Attività di Fisica Computazionale, at Banco di Sardegna (Swift code: SARDIT3S100), Sede di Cagliari, Codice ABI 1015/7 - CAB 04800/9.

Series Chairman: prof. A. Baldereschi - EPFL Lausanne

Workshop Chairman: prof. F. Meloni - INFM and Università di Cagliari

Scientific Secretariat:

dr. F. Bernardini, dr. V. Fiorentii
dr. P. Ruggerone, dr. A. Satta
INFM and Università di Cagliari

7.3.4 Conference on "Open questions in understanding the superconducting and normal state properties of MgB2"

University of Rome, La Sapienza, Italy

02 - 04 July, 2003

Supported by ESF Psi-k Programme

We would like to remind you about the conference "Open questions in understanding the superconducting and normal state properties of MgB2", to be held at the University Rome, La Sapienza, Italy, 02 - 04 July 2003. The aim of this meeting is to give an overview of the current knowledge of MgB2 and to define new theoretical avenues for overcoming the limitations in our theoretical understanding. The emphasis will be given to the issues still representing challenges to the currently accepted theoretical models, including, but not limited to the following:

Effect of impurity scattering
Effects of various dopings
Normal state transport
Role of electron-two phonon coupling
Nonadiabatic effects

There will be about 25 invited talks, and a limited number of contributed talks and poster presentations selected by the organizers based on the submitted abstracts. Preliminary list of invited speakers includes

J. An (LBNL, USA), O.K. Andersen (Stuttgart, Germany), M. d'Astuto (Grenoble, France), K.P. Bohnen (Karlsruhe, Germany), P. Canfield (Ames, USA), A.D. Caplin (London, UK), E. Cappelluti (Rome, Italy), A. Carrington (Bristol, UK), S.L. Drechsler (Dresden, Germany), M.R. Eskildsen (Geneva, Switzerland), A.A. Golubov (Twente, The Netherlands), R.S. Gonnelli (Torino, Italy), M. Iavarone (Argonne, USA), A.G.M. Jansen (Grenoble, France), A. Junod (Geneva, Switzerland), S. Massidda (Cagliari, Italy), I.I. Mazin (Washington, USA), E. Pavarini (Pavia, Italy), W. Pickett (Davis, USA), P.Postorino (Rome, Italy), A. V. Sologubenko (Zurich, Switzerland), S. Savrasov (Newark, USA), T. Masui (Tokyo, Japan).

We are looking forward to an exciting meeting with an intensive exchange of results and

ideas in an informal and inspiring atmosphere. There is no registration fee, and limited financial assistance will be available for young scientists and researchers from developing countries, on an individual basis. If you wish to participate in the conference, please submit your contribution to mgb2@fkf.mpg.de .

More information about the conference, as well as the contact information, can be found at:

http://www.mpi-stuttgart.mpg.de/conf/mgb2 .

Sincerely,

The Organizing Committee

7.3.5 Conference on 'AB-INITIO MANY-BODY THEORY FOR CORRELATED ELECTRON SYSTEMS'

25 - 29 August 2003

Miramare, Trieste, Italy

We would like to announce and encourage participation in the Conference on 'Ab-initio many body theory for correlated electron systems' to be held at the Abdus Salam International Centre for Theoretical Physics (ICTP) in Trieste, Italy from 25 to 29 August 2003. This conference is supported by the ICTP and Psi-k. Its overall aim is to communicate the latest technical developments in ab-initio many body calculations and to illustrate this on a few selected applications. The technical topics which will be stressed at this conference are:

Dynamical mean field theory (DMFT) and electronic structure calculations, with applications to d- and f-electron materials;
Recent developments on the GW approximation. This includes in particular issues related to self-consistency, and recent efforts to combine GW with DMFT towards a first-principles electronic structure method for strongly correlated electron systems;
Latest developments and applications of Quantum Monte Carlo methods;
Developments in Density Functional Theory and its implementation: time dependent DFT, "downfolding" on a few-orbital hamiltonian, etc...

Applications of these methods to materials-specific calculations will include:

- transition metals and their oxides;
- f-electron materials;
- fullerenes.

In addition, topical sessions on experimentally active field will be organized on:

- Spectroscopies;
- high pressure studies;
- ferromagnetic superconductors;
- magnetic semiconductors and nanoelectronics, including transport.

CONFIRMED SPEAKERS include:

O.K. Andersen, F. Aryasetiawan, M. Capone, T. Dietl, S. Erwin, iC. Filippi, R. Godby, E.K.U. Gross, K. Held, T. Kotani, G. Kotliar, C. Lambert, T. Le Bihan, A. Liechtenstein, I. Mertig, R. Needs, W. Pickett, M. Rozenberg, A. Rubio, S.Y. Savrasov, A. Schindlmayr, T. Schultess, T. Schulthess, A. Sekiyama, A. Svane, K. Syassen, N. Vast, D. van der Marel, G. Zarand, N.E. Zein, S. Zhang.

ADDITIONAL INFORMATION, REGISTRATION INFORMATION AND A PRELIMINARY PROGRAM can be found on the web at:

```
http://www.ictp.trieste.it/~smr1512/
```

Antoine Georges and Walter Temmerman

8 General Workshop/Conference Announcements

8.1 20th Nordic Semiconductor Meeting 2003

2nd Circular

Tampere/Tammerfors, Finland

Mon-Wed, 25-27 August 2003

http://www.suvisoft.fi/serv/nsm03/

This is 20th in a series of Nordic Semiconductor Meetings focusing on semiconductors, devices, systems and characterization methods. This meeting has the tradition to bring together Nordic researchers and semiconductor specialists.

Feel free to further distribute this circular to your colleagues and others possibly interested. Download the poster (First call for papers) from

http://www.suvisoft.fi/serv/nsm03/

The scope of the Meeting is:

Semiconductors
Devices
Systems
Characterization methods

The confirmed invited speakers include:

Kjeld Pedersen, Aalborg University
"Growth and characterization of thin crystalline metal layers on silicon surfaces"

Bengt G. Svensson, University of Oslo
"Defects and Diffusion in SiGe and SiC"

Magnus Willander, CTH
"Silicon-germanium strained layers and heterostructures"

Mikael Östling, KTH
Title to be confirmed

Oleg Okhotnikov, TUT
"Nonlinear semiconductor mirrors: technology and applications"

Mohammed Ismail, Spirea Ab
"Radio design for 3G and 4G wireless chipsets"

NN, STMicroelectronics
Title to be confirmed

Helena Pohjonen, Nokia
"Semiconductor Technologies in Future Portable Cellular Electronics"

Jyrki Kaitila, Infineon
Title to be confirmed

Organizing and Program Committee:

Markus Pessa	Chairman	Markus.Pessa@orc.tut.fi
Risto Nieminen	Program Chair	
Tapio Rantala	Secretary	Tapio.Rantala@tut.fi
Jouni Heleskivi		
Pekka Kuivalainen		
Kimmo Saarinen		
Heikki Seppä		
Sergey Vainshtein		

Secretariat

Tapio Rantala	Tapio.Rantala@tut.fi
Pirjo Kuhanen	Pirjo.Kuhanen@orc.tut.fi
Pekka Pöyhönen	Pekka.Poyhonen@orc.tut.fi
Anne Viherkoski	Anne.Viherkoski@orc.tut.fi

For more details see http://www.suvisoft.fi/serv/nsm03/, which will be continuously updated to provide information about invited speakers, detailed program, registration, accommodation and our sponsors.

8.2 CMD-EPS 2004

The 20th General Conference

of the Condensed Matter Division of the European Physical Society

Prague, July 19 - 23, 2004

As you may already know, the Czech Physical Society was entrusted with organizing the 20th General Conference of the Condensed Matter Division of the European Physical Society in Prague in July 2004. Prague Congress Center has been reserved as the conference site; it is ideally suited for a conference of the size and format well established for the EPS CMD General Conferences by now. Other preparatory work is also under way. All relevant information about the conference is accessible on

http://cmd.karlov.mff.cuni.cz/CMD/

We turn to you on behalf of the organizers and of the International Program Committee asking you to kindly make your proposals concerning the scientific program. The conference should serve two basic purposes. On the one hand to provide a competent account of the state and of important contemporary developments of the Condensed Matter Physics, on the other hand to be a broad forum giving an ample opportunity for all participants to join the discussions and to present their results and opinions.

The International Program Committee thus invites proposals for plenary invited talks and for focused sessions, both based on suggesting competent invited speakers, as well as proposals for minicolloquia topics and organizers. To facilitate submission and processing of the proposals please make use of the Proposal Forms, on line, or off-line, we have prepared at the web address given above. If justified, please do not hesitate to propose yourself or your close colleagues.

We hope to hear from you soon (the deadline for proposals has been set to Friday June 13, 2003), and to welcome you in Prague next year.

Yours sincerely,

Bedrich Velicky	Vladimir Sechovsky
Chair, International	Conference
Program Committee	Chair

8.3 Bukhara International Workshop and Conference

QUANTUM COMPLEXITIES IN CONDENSED MATTER

An International Workshop and Conference

21-28 August, 2003

Bukhara, Uzbekistan

Quantum Complexities in Condensed Matter provides a forum for the discussion of forefront theoretical and experimental research on Quantum Phase Transitions, Low Dimensional Magnetism, Quantum Ferroelectrics, Thin Film Magnetism, Unconventional Superconductivity, Heavy Fermions, Organics, Correlated Oxides, and The Bose-Einstein Condensate.

Quantum Complexities in Condensed Matter will bring together the latest experimental results with new theoretical insights in order to further understanding of the effects of strong electronic correlations and the nature of the emergent complex quantum ground states.

Bukhara with its millennia long intellectual tradition in science, art and philosophy is an ideal setting to bring together thinkers from east and west. This Silk Road city has documented history of 2500 years but has featured in eastern folklore for a period twice as long as that. Bukhara, home of fire worshipping Sogdians followed by Turkic and Persian dynasties who set up world-renowned universities and schools, began to flower as a hub of intellectual renaissance in the sixth century. Bukhara reached a peak from the eighth through the eleventh century, when it produced people like Avicenna and Rudaki. Bukhara has played a unique role in bringing eastern and western thought together as its intellectual traditions have represented a confluence of Greek, Chinese, Indian, Turkic, Persian and Arab ideas.

We hope that this backdrop of intellectual plurality will set the stage for a new and innovative understanding of properties of correlated electronic matter.

ABSTRACT DEADLINE: June 15, 2003

ORGANIZERS: S.S. Saxena (Cambridge), D.J. Singh (Washington).

DETAILS: See the web site: http://spider.phy.cam.ac.uk/saxena/bukharaneil2.htm

8.4 Meeting on 'Molecular and Solid State Quantum Chemistry'

Daresbury Laboratory, UK

9-10 June, 2003

On the 9th and 10th June 2003 we will be holding a meeting in honour of Dr Vic Saunders on 'Molecular and Solid State Quantum Chemistry' at Daresbury Laboratory, UK where Vic has been a senior research scientist since 1978.

Vic's career in research spans many years during which time he has made many contributions to the development of molecular and solid state quantum chemistry. The meeting is designed to reflect these interests and will take the form, principally, of invited talks delivered by Vic's collaborators and colleagues and will include

Prof. Henry Schaefer	University of Georgia
Prof. Nicholas Handy	University of Cambridge
Prof. Ian Hillier	University of Manchester
Prof. Peter Taylor	University of Warwick
Prof. Brian Sutcliffe	Universite Libre de Bruxelles
Dr. Anthony Stone	University of Cambridge
Prof. Peter Knowles	University of Birmingham
Prof. Michel Dupuis	PNL
Prof. Peter Pulay	University of Arkansas
Prof. Joop van Lenthe	University of Utrecht
Prof. David Dixon	PNL
Dr. Robert Harrison	ORNL
Prof. Harry King	University of Buffalo
Prof. Nicholas Harrison	CCLRC Daresbury Laboratory
Dr. Steve Wilson	CCLRC Rutherford Appleton Laboratory
Prof. Roberto Dovesi	Universit Degli Studi di Torino
Prof. Cesare Pisani	Universit Degli Studi di Torino
Dr. Bill Macrodt	University of St. Andrews

For further details about this event, and for registration information please use the link below

http://www.cse.clrc.ac.uk/events/mssqc/index.htm .

I look forward to seeing you at the meeting

Yours,

Prof. Nicholas Harrison
Head Computational Materials Science Group, CCRLC
Prof. of computational materials science, Imperial College London
email: nicholas.harrison@ic.ac.uk

8.5 2003 MRS FALL MEETING: Symposium DD

Call for Papers

Actinides: Basic Science, Applications, and Technology
December 1-5, 2003–Boston, MA

The Materials Research Society is pleased to announce that the Call for Papers for the 2003 MRS Fall Meeting is now available online at:

http://www.mrs.org/meetings/fall2003

Abstracts Due– June 19, 2003 for online submissions, June 5, 2003 for submissions by fax or mail.

Scope

Actinides are an important, if sometimes unwanted, part of highly technological societies. Actinide materials pose an extreme scientific challenge to the materials research community. Their complex electronic structure results in many abnormal properties that even today are not well understood, if at all. The focus will be fundamental actinide science and its role in resolving technical challenges posed by actinide materials. Both basic and applied experimental approaches, as well as theoretical modeling and computational simulations, are planned to be part of the symposium.

A proceedings book is planned for this symposium. It is anticipated that the symposium will take place over a four day period.

Topics of particular interest include the following:

- fundamental physical properties
- theory, calculations and simulations
- synchrotron-radiation-based investigations
- waste form materials science
- solution chemistry
-separation science
-electronic and magnetic properties and their relationship to physical structure
- synthetic methods
-optical properties
- behavior under extreme conditions such as high pressures
- heavy element research
- environment/remediation

Partial Invited Speaker List (in alphabetical order):

M. Antonio, ANL, Chicago, IL
T. Fryberger, DOE, Germantown, MD
S. Hecker, LANL, Los Alamos, NM
B. Johansson, Uppsala University, Uppsala, Sweden
G. Kotliar, Rutgers University, Piscataway, NJ
G. Lander, ITU, Karlsruhe, Germany
B. Maple, UCSD, La Jolla, CA
J. Sarrao, LANL, Los Alamos, NM
W. Wolfer, LLNL, Livermore, CA

Symposium Organizers:

James G. Tobin, Lawrence Livermore National Laboratory
John Joyce, Los Alamos National Laboratory
Malcolm F. Nicol, University of Nevada Las Vegas
David Shuh, Lawrence Berkeley National Laboratory
Lynda Soderholm, Argonne National Laboratory

8.6   NanoteC'03 Conference

NanoteC'03, Nanotechnology in carbon and related materials

27-30th August 2003

University of Sussex, Brighton, UK

http://www.hpc.susx.ac.uk/nanotec/

This is the fifth international conference sponsored by the British Carbon Group (http://www.hpc.susx.ac.uk/BCG/), this year in collaboration with the Royal Microscopical Society (http://www.rms.org.uk/), with the aim of promoting carbon science in the nano scale as, for example, fullerenes, nanotubes, nanowires, sp^3 forms, etc.

The NanoteC conferences are renowned for their relaxed and friendly atmosphere, with emphasis on discussion and participation. We are endeavouring to achieve as much student participation as possible, and we anticipate that the keynote talks will be strongly influential on the next generation of nanotechnology scientists. Full details are on the Website.

This year the conference has sessions on microscopy, synthesis, devices and carbon based electronics, composites, and theory and modelling.

Contact: Dr Tony Wickham (confer@globalnet.co.uk)

Deadlines: Abstract submission is the 20th July 2003, and for registration is 1st August.

8.7 International Workshop on Ferromagnetic Semiconductors & Synchrotron Radiation

Pre Announcement

SRS Daresbury Laboratory, UK, 11 - 12 September 2003

Diluted magnetic semiconductors (DMS) are expected to play an important role in interdisciplinary materials science and future spintronics because the integration of charge and spin degrees of freedom will deliver new types of devices for information storage and processing. This workshop is to introduce these new materials as well as to report on state-of-art results (both experiment and theory). The emphasis will be on the exploitation of powerful techniques derived from magnetic x-ray dichroism using synchrotron radiation, offering vector magnetometry which is site, element and chemical specific.

Venue: Tower Seminar Room, SRS Daresbury Laboratory, Warrington, Cheshire, UK.

Travel info: `http://srs.dl.ac.uk/ulo/Route_map.html`

Scientific organiser: Gerrit van der Laan

Conference office: Sue Waller

Tentative programme

Thursday 11 September 2003

14:00	G. van der Laan (Daresbury)	Opening remarks
14:10	Tomas Jungwirth (Austin/Prague)	General introduction
15:10	Oliver Rader (Bessy)	Photoemission on DMS
15:40	Tea/Coffee break	
16:10	Bryan Gallagher (Nottingham)	Materials development
17:10	Tomasz Story (Warsaw)	New spintronic developments
18:10	End of session	
17:30	Dinner	

Friday 12 September 2003

09:00	Russell Cowburn (Durham)	Magnetic nanodots special
10:00	Ulrich Hillebrecht (Karlsruhe)	XMCD on DMS
10:30	Coffee break	
11:00	Hermann Durr (Bessy)	Femtosecond dynamics
12:00	Thomas Schulthess (ORNL)	Electronic state of DMS
13:00	Closing remarks	

For further announcements, watch

```
http://www.srs.ac.uk/srum/satellite_1.htm
```

The satellite workshop takes places immediately after the Synchrotron Radiation User Meeting. You might like to consider to participate also in the main SR User Meeting. For details see

(http://www.srs.ac.uk/srum/).

Meeting arrangements:

There will be no registration fee but you must provide your own accommodation and travel costs, and buy any tickets for meals. For reasons of limited site capacity and visitor safety it is possible that attendance numbers will have to be capped. An early registration is strongly advised, preferably using the online facilities:

```
http://www.srs.ac.uk/srum/satellite_1.htm
```

(available after 1 June).

Accommodation

If you would like us to book your hotel accommodation please indicate your requirements on the online form. Unless arranged otherwise, please be prepared to settle your own hotel account upon departure.

9   General Job Announcements

Post Doctoral Position

Department of Electrical Engineering

University of California, Riverside

Riverside, CA 92521-0204

April 10, 2003

Immediate opening for post-doctoral researcher with computational materials or computational chemistry background. Our immediate project is the modeling of oxidized Si/SiGe nanowires. For the longer term, we are interested in electron and phonon transport in heterogeneous metal/semiconductor/CNT/molecular systems. Candidates should have experience with DFT calculations, software, and code development. Experience with MD calculations is helpful. Funding is secure through Sept. 2004 with follow-on funding likely.

Contact:

Roger Lake
Associate Professor
Department of Electrical Engineering
University of California
Riverside, CA 92521-0425
Ph. 909-787-2122
rlake@ee.ucr.edu
 http://www.ee.ucr.edu/~rlake

POST DOCTORAL OPENING FOR COMPUTATIONAL QUANTUM CHEMIST/BAND THEORIST

Chemistry Department, Case Western Reserve University, Cleveland OH 44106, USA

The above position is soon to be available in the lab of Professor A. B. Anderson. The research will center on electron transfer theory and electro-catalytic reaction mechanisms with an emphasis on novel fuel cell electrodes. Both Gaussian and VASP methods will be used and familiarity with the VASP code would be very desirable.

The appointment will be for one year and may be extended contingent on mutual agreement. The stipend will be USD 30,000 or more depending on experience. Please apply to aba@po.cwru.edu with your cv and please arrange for three letters of recommendation to be sent. Phone: 216 368 5044; fax 216 368 3006.

Case Western Reserve University is one of several important scientific, cultural, and medical institutions in the University Circle area of Cleveland. If you are not familiar with it, please check it out on the web. Electrochemical research spans several departments at our University and the University is well known for research in this field. The successful candidate will benefit from possible interactions with groups in other departments here and at other universities and at companies.

Case Western Reserve University is an equal opportunity, affirmative action employer and encourages applications from women and minorities.

POSTDOCTORAL POSITION

Institut de Ciencia de Materiales de Barcelona (CSIC)
Barcelona, Spain

A postdoctoral position in the group of Pablo Ordejon and Eduardo Hernandez at the Institute of Materials Science of Barcelona (Spain) is available, starting inmediately.

The research topic is flexible, and can be defined according to the preferences and backgrouwnd of the candidate. However, strong involvement in ongoing projects of reactivity of organometallic compounds on metallic surfaces is a requirement.

The successful candidate should have a PhD in Physics, Chemistry or Materials Science, and have a strong background in first principles simulations. Preference will be given to candidates with experience in simulations of chemical reactions at surfaces.

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

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

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

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

Ph. D. Studentship

Physics Department of King's College, University of London, U.K.

A three year Ph.D. studentship is available from October 2003 at the Physics Department of King's College, University of London, for research on first principles simulations applied to nano- or bio-materials. Both UK and European Communities citizens are elegible.

For further details about projects, please email me at carla.molteni@kcl.ac.uk. For information about the formal application procedure, please contact the postgraduate tutor Dr Alison Mainwood at alison.mainwood@kcl.ac.uk.

The web site of King's College London, containing also information for perspective students is www.kcl.ac.uk.

Dr Carla Molteni
Physics Department
King's College London
Strand
London WC2R 2LS
United Kingdom

carla.molteni@kcl.ac.uk

PhD Studentship

ETH Zurich, Department of Materials, Laboratory of Crystallography

A 3-year PhD studentship is expected to open on 1 October 2003 in the Theory of Minerals at Extreme Conditions group at ETH Zurich. The research project is based on ab initio studies of Earth- and planet-forming materials. It will involve state-of-the-art simulation methods and results will have important implications in geophysics and planetary science. The candidate is expected to have obtained an MSc or equivalent degree in solid-state physics, chemistry, mineralogy, or crystallography. Familiarity with simulation methods is useful, but not necessary at this stage. The starting salary is 41,500 Swiss Francs (about 27,500 EUR) per year. Applications (containing contact details, CV or a description of research interests, and names of two referees) and requests for further information should be sent to:

Dr. A.R. Oganov
Laboratory of Crystallography
ETH Zurich, Zurich
CH-8092, Switzerland

E-mail: a.oganov@mat.ethz.ch.

PHD STUDENTSHIP

ROOM TEMPERATURE IONIC LIQUIDS

Atomistic Simulation Group at Queen's University Belfast

A three-year EPSRC PhD studentship is available from 1 October 2003 in the Atomistic Simulation Group at Queen's University Belfast. The project is to study, using atomistic simulation, the behaviour of room temperature ionic liquids in the vicinity of charged oxide surfaces used for solar cell applications. The succesful candidate will work under the supervision of Dr J. Kohanoff and Prof. R. M. Lynden-Bell. For further details see:

http://titus.phy.qub.ac.uk/posts/index.html

or contact Dr Jorge Kohanoff (j.kohanoff@qub.ac.uk).

The studentship is open to citizens of any nationality, and covers University fees and subsistence (8000 Pounds in the first year, increasing to 10500 and 12000 in the second and third year). Applications including a CV, details of examination results, and the names and e-mail (or address) of two referees should be sent to Dr Jorge Kohanoff either by e-mail or post to the address below.

Deadline for receipt of applications is Friday, June 20th.

Dr Jorge Kohanoff
Atomistic Simulation Group
Queen's University Belfast
Belfast BT7 1NN
Northern Ireland

Phone : +44 (0) 28 9027 3770
E-mail: j.kohanoff@qub.ac.uk

Postdoctoral Fellow

Lawrence Livermore National Laboratory, CA

A position of a post-doctoral fellow is available in the area of studying correlated electrons in electronic structure calculations. The position is available immediately. The work has both conceptual and computational aspects connected with the possibility of treating correlated electrons in solids through the direct study of two-particle states (rather than single-particle states). This involves the extension of LDA to two-particle densities and addressing conceptual issues that attend to such extension. It also requires testing ideas using first simple model Hamiltonians (1-D, TB) with extensions to realistic systems to follow. Candidate should have a good grasp of traditional methodology (DFT), be exposed to many-body theory, and be able to work on the development and implementation of codes.

Antonios "Tony" Gonis
Lawrence Livermore National Laboratory
P.O. Box 808, L-353
Livermore, CA 94550
Phone: (925) 422-7150
FAX: (925) 423-7040

POSTDOCTORAL POSITION

CONDENSED MATTER THEORY/QUANTUM COMPUTING

IOWA STATE UNIVERSITY and AMES LABORATORY

The research involves analytical and numerical studies of quantum many-spin systems (decoherence and dephasing processes). The emphasis is on actual solid-state systems which are under consideration for the implementation of quantum computation. The candidate is expected to have experience in analytical and/or numerical approaches to quantum many-body problems, and, preferably, knowledge of basic quantum information theory. The salary is is in the range of USD 35k to USD 40k, depending on relevant experience. Applications, CV, and recommendation letters should be sent to

V. V. Dobrovitski,
Physics Department,
Iowa State University,
Ames, IA 50011
(or email at: slava@ameslab.gov)

or to

B. N. Harmon,
Physics Department,
Iowa State University,
Ames, IA 5001
(or email at: bnharmon@iastate.edu).

Tenure-track faculty position
NSERC University Faculty Award program

Département de physique
Faculté des arts et des sciences
Université de Montréal

The Département de physique, Université de Montréal, invites applications for a tenure-track faculty position at the assistant or early associate professor level from women for submission to the NSERC University Faculty Award program. This program aims at increasing the representation of women faculty in Canadian universities and is limited to Canadian citizens and permanent residents (cf. `http://www.nserc.ca/guide/c7_e.htm`).

The candidate will be expected to pursue a vigorous research program in one of the priority domains of the department, in particular:

- plasma physics, plasma -material interactions; material synthesis and nano-materials; molecular electronics/photonics, etc.;

- molecular biophysics, microscopy, theoretical biophysics;

- particle astrophysics, dark matter; extragalactic astronomy, cosmology; stellar astrophysics.

Details on the areas of research of the department can be found at http://www.phys.umontreal.ca/. Applicants must have a Ph.D. degree, a record of outstanding research accomplishments and a commitment to excellence in teaching. The Université de Montréal offers competitive salaries together with a full spectrum of social benefits. Candidates should submit a curriculum vitae and a summary of the planned research programme (in hardcopy - e-mail submissions will not be accepted) and have three letters of recommendation sent by August 15, 2003 to :

Laurent J. Lewis, Chair
Département de physique
Université de Montréal
P.O. Box 6128, Station centre-ville
Montréal, Québec
Canada H3C 3J7

The Université de Montréal is committed to equal employment opportunity for women and to employment equity.

10 Abstracts

Stoichiometry of Fe$_{3-\delta}$O$_4$(111) ultrathin films on Pt(111)

P. Morrall, F. Schedin

Surface Science Research Centre and Chemistry Department,
University of Manchester, Manchester M13 9PL, U.K.

G. S. Case, M. F. Thomas

Department of Physics, University of Liverpool, Liverpool L69 3BX, U.K.

E. Dudzik, G. van der Laan

Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, U.K.

Abstract

The composition and magnetic properties of two types of ultrathin Fe$_{3-\delta}$O$_4$(111) film grown epitaxially on Pt(111) have been characterised using conversion electron Mössbauer spectroscopy (CEMS) and x-ray magnetic circular dichroism (XMCD). CEMS data from both films indicate that the magnetic moments lie in-plane and that a paramagnetic contribution is present which is not seen in spectra of bulk magnetite samples. The XMCD results are in good agreement with theoretical calculations, enabling the stoichiometry of the films to be determined as Fe$_3$O$_4$ and Fe$_{2.91}$O$_4$. The concentrations of both the tetrahedral Fe^{3+} and octahedral Fe^{2+} ions are reduced in the non-stoichiometric film, the decrease in the tetrahedral site probably being due to disorder. CEMS consistently yields a high tetrahedral/octahedral ratio of $\sim 0.7 : 1$, probably because of a contribution from a nonstoichiometric FeO interface layer.

X-ray resonant magnetic reflectivity from Fe/Ce multilayers

N. Jaouen

ESRF, 6 Rue Jules Horowitz, F-38043 Grenoble, France

J.M. Tonnerre, D. Raoux

CNRS, Lab Cristallog, F-38042 Grenoble, France

D, M. Muenzenberg, W. Felsch

Univ Gottingen, I Phys Inst, D-37073 Gottingen, Germany

A. Rogalev, N. Brookes

ESRF, F-38043 Grenoble, France

H. Durr, G. van der Laan

Daresbury Laboratory, Warrington WA4 4AD, Cheshire, UK

Abstract

We report on X-ray resonant magnetic reflectivity (XRMR) at the Ce L_2 and M_4, M_5 edges in an ex-situ grown Fe/Ce multilayer. We show that the measurement of the magnetic contribution to the intensities reflected at low angles allows us to investigate the profile of the Ce $5d$ and $4f$ magnetization. The calculated XRMR signals indicate that the Ce moments have a non-collinear structure.

Contact person: G. van der Laan (g.vanderlaan@dl.ac.uk)

Ab initio calculation of tensile strength in iron

M. Friák[1,2], M. Šob[1], V. Vitek[3]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic

[3] *Department of Materials Science and Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

A tensile test in ferromagnetic iron for loading in [001] and [111] directions is simulated by ab initio electronic structure calculations using all-electron full potential linearized augmented plane wave method (FLAPW) within generalized gradient approximation (GGA). The theoretical tensile strengths and Young moduli of ferromagnetic iron are determined and compared with those of other materials. The magnetic and elastic behaviour of iron under uniaxial tensile loading is discussed in detail and compared with the results for isotropic tension (i.e. for negative hydrostatic pressure). Marked anisotropy of theoretical tensile strength in [001] and [111] direction is explained in terms of higher-symmetry structures present or absent along the deformation paths.

Theoretical strength and onset of yielding in nanoindentation

M. Šob[1], M. Friák[1,2], V. Vitek[3]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic

[3] *Department of Materials Science and Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

Quantum-mechanical (ab initio) approach for determining theoretical (ideal) tensile and shear strength in metals and intermetallics is briefly outlined and, as an example, tensile test for defect-free $MoSi_2$ is simulated. Theoretical values of tensile and shear strength are compared with those obtained from loading of whiskers and from nanoindentation experiments. As nanoindentation tests can sample defect-free volumes, the onset of yielding should correspond to theoretical shear strength. Possible sources of discrepancies between the measured maximum shear stress in nanoindentation experiments and theoretical values as well as corresponding corrections are discussed. The calculated or measured values of theoretical strength may subsequently serve as input parameters to a quantitative and predictive model, based on the properties of dislocation interactions, that describes the relationship between the yield behaviour and length-scale effects in the nanoscale regime.

PACS Numbers: 71.20.Be, 61.50.Ks, 61.66.Dk, 62.20.Dc, 62.20.Fe

Contact person: Mojmír Šob (mojmir@ipm.cz)

Nanoindentation and theoretical strength in metals and intermetallics

M. Šob[1], D. Legut[1,2], M. Friák[1], J. Fiala[2], V. Vitek[3], J. Hafner[4]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic*

[2] *Department of Chemistry of Materials, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, CZ-612 00 Brno, Czech Republic*

[3] *Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.*

[4] *Institut für Materialphysik and Center for Computational Materials Science, University of Vienna, Sensengasse 8/12, A-1090 Vienna, Austria*

Abstract

Applications of ab initio electronic structure methods is illustrated by calculation of theoretical tensile strength in $MoSi_2$ and WSi_2. Simulation of nanoindentation process from the first principles is briefly described.

Phase diagram calculation in Co-Cr system using ab-initio determined lattice instability of sigma-phase

J. Houserová[1], J. Vřešťál[1,2], M. Friák[1], M. Šob[1]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic*

[2] *Institute of Theoretical and Physical Chemistry,Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic*

Abstract

The calculations of phase equilibria in the Co-Cr system were performed using the CALPHAD method on the basis of a new two-sublattices model of sigma phase. This model enables us to utilise the results of ab initio calculations of total energy differences between the sigma phase structure and the Standard Element Reference (SER) structures of pure metal at the relaxed lattice parameters ($\Delta^0 E_i^{\sigma-SER}$). Total energies were calculated by Full-Potential Linear Augmented Plane Waves (FLAPW) method in the General Gradient Approximation (GGA). The entropy contribution to the Gibbs energy of the pure elements in the sigma phase structure, and the excess Gibbs energy of mixing of the sigma phase were adjusted to the experimental phase equilibrium data.

PACS Numbers: 61.66.Dk, 71.20.Be, 82.60.Lf

Ab initio calculations of lattice stability of sigma-phase and phase diagram in the Cr-Fe system

J. Houserová[1], M. Friák[1], M. Šob[1], J. Vřešťál[1,2]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic*

[2] *Institute of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic*

Abstract

Total energy of pure metals in the sigma-phase structure and in the standard element reference (SER) structure were calculated by full-potential linear augmented plane waves method in the general gradient approximation at the equilibrium volume of all phases. Relaxation of lattice parameters of sigma-phase and SER structure were performed. The difference of total energy of sigma-phase and of standard element phase for pure constituents ($\Delta^0 E_i^{\sigma-SER}$) was used in a new two-sublattice model of sigma-phase, which was subsequently employed for calculation of phase diagram.

Entropy term of Gibbs energy of elements in sigma-phase structure and excess Gibbs energy of mixing of sigma-phase have still to be adjusted to the experimental phase equilibrium data. This procedure was tested on the Fe-Cr system.

PACS Numbers: 61.66.Dk, 71.20.Be, 82.60.Lf

Contact person: Jana Houserová (houserova@ipm.cz)

Ab initio calculations of elastic and magnetic properties of Fe, Co, Ni, and Cr crystals under isotropic deformation

M. Černý[1], J. Pokluda[1], M. Šob[2], M. Friák[2], P. Šandera[1]

[1] *Institute of Engineering Physics, Faculty of Mechanical Engineering,*
Brno University of Technology, Technická 2, CZ-616 69 Brno, Czech Republic
[2] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

Abstract

Ab initio electronic structure calculations of the ideal strength of Fe, Co, Ni, and Cr under isotropic tension were performed using the linear muffin-tin orbital method in the atomic sphere approximation. Magnetic ordering was taken into account by means of a spin-polarized calculation. Two approximations for the exchange-correlation term were employed: namely, the local (spin) density approximation and the generalized gradient approximation. Computed values of equilibrium lattice parameters, bulk moduli, and magnetic moments were compared with available experimental data. The stability of the ground-state structure in the tensile region was assessed via comparison of its total energy and enthalpy with those of some other structures. No instabilities were found before reaching the inflection point on the total energy versus volume curve and the stress related to this point was therefore considered to be the ideal strength. PACS Numbers: 61.50.Ah, 61.66.Bi, 71.15.Mb, 75.50.Bb

Multiple Si=O Bonds Effects at Silicon Cluster Surfaces

Marcello Luppi

INFM-S³ and Dipartimento di Fisica,
Università di Modena e Reggio Emilia,
I-41100 Modena, Italy

Stefano Ossicini

INFM-S³ and Dipartimento di Scienze e Metodi dell'Ingegneria,
Università di Modena e Reggio Emilia,
I-42100 Reggio Emilia, Italy

Abstract

A first principle investigation of the effects of multiple Si=O bond bonds at the surface of silicon-based clusters has been carried out. Total energy pseudopotential calculations within density functional theory have been applied varying systematically the number of double bonds at the clusters surface. A non linear reduction of the energy gap with the double bonds number is found, providing a consistent interpretation of the photoluminescence red shift in oxidized porous silicon samples. Moreover an explanation of the results on the single quantum dots photoluminescence band width is proposed.

A pressure-induced phase of NaAlH$_4$: A potential candidate for hydrogen storage ?

P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvåg, and A. Kjekshus
Department of Chemistry, University of Oslo,
Box 1033, Blindern, N-0315, Oslo, Norway.

Abstract

The electronic structure and structural stability of the technologically interesting material NaAlH$_4$ are studied using an *ab initio* projected augmented plane-wave method for different possible structure modifications. We predict that α-NaAlH$_4$ converts to β-NaAlH$_4$ at 6.43 GPa with a 4 % volume contraction. Both modifications have nonmetallic character with finite energy gaps, the calculated bandgap for β-NaAlH$_4$ being almost half of that for the α-phase. β-NaAlH$_4$ stores hydrogen more volume efficient than the α-phase and would if stabilized at ambient conditions be an interesting candidate for further studies with regard to hydrogen absorption/desorption efficiency.

Crystal structure of KAlH$_4$ from first principle calculations

P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg
Department of Chemistry, University of Oslo,
Box 1033, Blindern, N-0315, Oslo, Norway.

Abstract

The crystal structure of KAlH$_4$ is determined by the first principle projected augmented plane wave method taking different possible structural arrangements into consideration. From the total energy it is concluded that KAlH$_4$ crystallizes in the orthorhombic KaGaH$_4$-type structure (space group *Pnma*) with unit-cell dimensions $a = 9.009$, $b = 5.767$, $c = 7.399$ Å. A metastable modification with α-NaAlH$_4$-type structure is predicted in energetic close proximity to the stable phase. The electronic structure show that KAlH$_4$ has non-metallic character with a band gap of approximately 5.5 eV.

Prediction of large polar Kerr rotation in the Heusler-related alloys AuMnSb and AuMnSn

Laila Offernes, P. Ravindran, and A. Kjekshus
Department of Chemistry, University of Oslo,
Box 1033, Blindern, N-0315, Oslo, Norway

Abstract

Theoretical spectra for the magneto-optical Kerr effect (MOKE) have been obtained for the Heusler-related alloys AuMnSb and AuMnSn, and repeated calculations are performed for the isostructural PtMnSb phase. Using experimental lattice constants, FPLMTO calculations predict a Kerr rotation of around $-1°$ in the $0.5-2$ eV region for AuMnSb and AuMnSn. Electronic structure calculations indicate that half-metallic behavior can be induced on hole doping of AuMnSb and electron doping of AuMnSn.

Ground- and excited-state properties of inorganic solids from full-potential density- functional calculations

P. Ravindran, R. Vidya, P. Vajeeston, A. Kjekshus, and H. Fjellvåg

Department of Chemistry, University of Oslo,

Box 1033, Blindern, N-0315, Oslo, Norway.

Abstract

The development in theoretical condensed-matter science based on density-functional theory (DFT) has reached a level where it is possible, from "parameter-free" quantum mechanical calculations to obtain total energies, forces, vibrational frequencies, magnetic moments, mechanical and optical properties and so forth. The calculation of such properties are important in the analyses of experimental data and they can be predicted with a precision that is sufficient for comparison with experiments. It is almost impossible to do justice to all developments achieved by DFT because of its rapid growth. Hence, it has here been focused on a few advances, primarily from our laboratory. Unusual bonding behaviors in complex materials are conveniently explored using the combination of charge density, charge transfer, and electron-localization function along with crystal-orbital Hamilton-population analyses. It is indicated that the elastic properties of materials can reliably be predicted from DFT calculations if one takes into account the structural relaxations along with gradient corrections in the calculations. Experimental techniques have their limitations in studies of the structural stability and pressure-induced structural transitions in hydride materials whereas the present theoretical approach can be applied to reliably predict properties under extreme pressures. From the spin-polarized, relativistic full-potential calculations one can study novel materials such as ruthenates, quasi-one dimensional oxides, and spin-, charge-, and orbital-ordering in magnetic perovskite-like oxides. The importance of orbital-polarization correction to the DFT to predict the magnetic anisotropy in transition-metal compounds and magnetic moments in lanthanides and actinides are emphasized. Apart from the full-potential treatment, proper magnetic ordering as well as structural distortions have to be taken into account to predict correctly the insulating behavior of transition-metal oxides. The computational variants LDA and GGA fail to predict insulating behavior of Mott insulators whereas electronic structures can be described correctly when correlation effects are taken into account through LDA+U or similar approaches to explain their electronic structures correctly. Excited-state properties such as linear optical properties, magneto-optical properties, XANES, XPS, UPS, BIS, and Raman spectra can be obtained from accurate DFT calculations.

Raman- and IR-active phonons in superconducting and non-superconducting rare-earth transition-metal borocarbides from full-potential calculations

P. Ravindran[1], P. Puschnig[2], C. Ambrosch-Draxl[2], L. Nordström[2], A. Kjekshus[1],
H. Fjellvåg[1], and B. Johansson[3]

[1] *Department of Chemistry, University of Oslo,*
Box 1033, Blindern, N-0315, Oslo, Norway.
[2] *Institut für Theoretische Physik, University Graz,*
Universitätsplatz, 5 A-8010 Graz, Austria
[3] *Condensed Matter Theory Group, Department of Physics, Uppsala University,*
Box 530, 75121, Uppsala, Sweden

Abstract

Ab-initio frozen-phonon calculations were performed for superconducting YNi_2B_2C and $LuNi_2B_2C$ and non-superconducting $LaNi_2B_2C$ and YCo_2B_2C to establish the phonon frequencies for all Raman- and IR-active optical $q = 0$ modes using the generalized-gradient-corrected full-potential linear augmented plane-wave method. From a series of atomic force calculations the shape of the phonon potential is established. Our calculated Raman-active phonon frequencies are found to be in very good agreement with the available Raman-scattering measurements. In the case of IR-active phonons there are no experimental frequencies available and our theoretical study is the first report for these series. The Raman-scattering intensities for all Raman-active modes of YNi_2B_2C are determined allowing a detailed comparison between theoretical and experimental Raman spectra. The changes in the electronic structure introduced by the phonon modes are also analyzed. Although the calculated electronic structure of these materials has three-dimensional character we found a large anisotropy in the optical dielectric function due to the layered nature of the crystal structure.

Ab initio lattice dynamics and structural stability of MgO

Artem R. Oganov[1], Michael J. Gillan[2], G. David Price[1]

[1]*Department of Earth Sciences, University College London,*
Gower Street, London WC1E 6BT, U.K.
[2]*Department of Physics and Astronomy, University College London,*
Gower Street, London WC1E 6BT, U.K.

Abstract

Using density-functional perturbation theory, we have studied lattice dynamics, dielectric and thermodynamic properties, and P-T stability fields of the NaCl- ("B1") and CsCl- ("B2") structured phases of MgO. The results compare well with available experiments and resolve the controversy between earlier theoretical studies. We predict that at all conditions of the Earth's mantle the B1-structure is stable. Static calculations predict the B1-B2 transition to occur at 490 GPa; zero-point vibrations lower this pressure by 16 GPa. The B2-structured phase is dynamically unstable below 110 GPa, but becomes dynamically stable at higher pressures. On the contrary, the B1 phase does not display soft modes at all of the studied pressures. MgO remains an insulator up to ultrahigh pressures: we predict metallisation of the B2-structured phase of MgO at 20.7 TPa.

Reconstruction and magnetic structure of ultrathin γ-Fe films on Cu(111)

D. Spišák and J. Hafner

Institut für Materialphysik and Center for Computational Materials Science,
Universität Wien, Sensengasse 8, A-1090 Wien, Austria

Abstract

We report *ab initio* investigations of the magnetic structure and reconstruction of ultrathin films of γ-Fe on Cu(111) substrates. For this system striking differences in the magnetic properties of films produced by thermal deposition and pulse laser deposition have been reported [J. Shen *et al.* J. Phys.: Condens. Matter **15**, R 1 (2003)]. We find that unlike for γ-Fe films on Cu(001), the geometrical and magnetic structures of Fe/Cu(111) films cannot be explained in terms of simple ferromagnetic or layered antiferromagnetic structures stacked along the surface normal. Instead, we find that the (bi)layer antiferromagnetic structures oriented along [001] representing the magnetic ground-state of Fe/Cu(001) films with four or more monolayers also determine the magnetic structure of Fe/Cu(111), even in the monolayer limit. In both cases, the stability of the bilayer antiferromagnetic structure is related to the stability of this type of magnetic ordering for nearly cubic or tetragonally distorted bulk γ-Fe. However, a ferromagnetic state of films with two to four monolayers is only about 6 meV/Fe atom higher in energy. Ferromagnetic ordering is coupled to strong monoclinic shear distortions in the bulk as well as in thin Fe/Cu(001) films. In Fe/Cu(111), however, the close packing in the layer leads to a quite large elastic energy for the large lateral displacements coupled to the ferromagnetic ordering so that the antiferromagnetic structure is marginally more stable from one to four monolayers. The coupling between magnetic structure and surface reconstruction could open a way for an experimental verification of our predictions.

Magnetism of ultrathin wires suspended in free space and adsorbed on vicinal surfaces

D. Spišák and J. Hafner

*Institut für Materialphysik and Center for Computational Materials Science,
Universität Wien, Sensengasse 8, A-1090 Wien, Austria*

Abstract

On the basis of total-energy calculations within density functional theory the possibility of magnetic ordering in ultrathin, one or two atom wide nanowires is studied. Specifically, we investigate nanowires composed of 5th and 6th row elements, which are nonmagnetic in the solid phase. At first, the unsupported straight wires are discussed and then, similar to experimental conditions, the wires are placed along step ledges of vicinal surfaces of copper and silver. Free-standing wires show only a weak tendency towards magnetic ordering at the equilibrium bond length. In analogy with their $3d$ homologues Mo, Tc, W, Re are found to order antiferromagnetically, Ru, Rh and Ir ferromagnetically. Surprisingly, ferromagnetism is also predicted for the early transition metals Zr and Ta and for the simple metals In and Tl. This picture is profoundly modified for supported wires, where the expansion of the bond length enforced through the epitaxial relationship with the substrate favors magnetic ordering but hybridization with the substrate electrons tends to quench magnetism. It turns out that wires on a Cu substrate prefer a ferromagnetic order, whereas on a Ag substrate most elements tend to antiferromagnetism. A second row of atoms added to the wires destroys the magnetism in wires on a Cu substrate, and reduces it in wires on a Ag substrate, except for the late transition metals (Rh, Ir) where an enhancement of magnetic moments is observed. Two possible growth modes of nanowires – a row-by-row growth and island growth – are explored. The results allow us to suggest that Ru, Rh, and Os wires on Ag stepped surfaces are the most promising systems in which magnetism could be verified experimentally.

Theoretical analysis of clock-reconstructed PdCu surface alloy

D. Spišák and J. Hafner

Institut für Materialphysik and Center for Computational Materials Science,
Universität Wien, Sensengasse 8, A-1090 Wien, Austria

Abstract

Ab-initio density-functional techniques (DFT) have been used to investigate the structural properties of PdCu surface alloys for which a clock reconstruction with p4g symmetry has been reported. Our calculations not only allow to discriminate between the various models proposed on the basis of the experimental data, they also elucidate the physical mechanism leading to the clock-rotated $p(2 \times 2)$-p4g surface structure. It is shown that free-standing square monolayers are unstable – not only relative to the most dense hexagonal lattice, but also relative to a square-triangle lattice characteristic of a p4g symmetry. This transformation is even barrierless or limited by a low energetic barrier. Whether this transformation will also occur in a surface layer depends on the coupling of the adlayer to the substrate – this explains why the reconstruction occurs only in the topmost layer of a bilayer PdCu alloy, but not in a single alloy layer. Our work demonstrates that DFT calculations provide a reliable tool for predicting surface reconstructions.

Insights into the function of silver as an oxidation catalyst by ab initio, atomistic thermodynamics

Wei-Xue Li,[1] Catherine Stampfl,[1,2] and Matthias Scheffler[1]

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

Faradayweg 4–6, D-14195 Berlin-Dahlem, Germany

[2] *School of Physics, The University of Sydney, Sydney 2006 Australia*

Abstract

To help understand the high activity of silver as an oxidation catalyst, e.g., for the oxidation of ethylene to epoxide and the dehydrogenation of methanol to formaldehyde, the interaction and stability of many different oxygen species at the Ag(111) surface has been studied for a wide range of coverages. Through calculation of the free energy, as obtained from density-functional theory and taking into account the temperature and pressure via the oxygen chemical potential, we obtain the phase diagram of O/Ag(111). Our results reveal that a *thin* surface-oxide structure is most stable for the temperature and pressure range of ethylene epoxidation and we propose it (and possibly other similar structures) contains the species actuating the catalysis. For higher temperatures, low coverages of chemisorbed oxygen are most stable, which could also play a role in oxidation reactions. For temperatures greater than about 775 K there are *no* stable oxygen species, except for the possibility of O atoms adsorbed at under-coordinated surface sites (i.e., imperfections, defects). At low temperatures ($\lesssim$ 400 K at atmospheric pressure), provided kinetic limitations can be overcome, thicker oxide-like structures are predicted. Due to their low thermal stability, however, they can be ruled out as playing an important role in the heterogeneous reactions under technical conditions. Bulk dissolved oxygen and a molecular ozone-like species adsorbed at a surface vacancy, as have been proposed in the literature, are found to be energetically unfavorable. The employed theoretical approach for calculating *free energies* and predicting the lowest energy structures in contact with species in the environment ("*ab initio*, atomistic thermodynamics"), affords investigation of a system that seemlessly connects standard ($T = 0$ K) DFT results, characteristic of "typical" theoretical surface science studies, through to those valid for the conditions of catalysis. Though the error bar of the noted theoretical temperatures is noticeable ($\pm \approx 55$ K), the identified trends and physical descriptions are useful.

The Pd(100)-($\sqrt{5} \times \sqrt{5}$)$R27^o$-O surface oxide revisited

M. Todorova[1], E. Lundgren[2], V. Blum[3], A. Mikkelsen[2], S. Gray[2],

J. Gustafson[2], M. Borg[2], J. Rogal[1], K. Reuter[1], J.N. Andersen[2], and M. Scheffler[1]

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

Faradayweg 4–6, D-14195 Berlin-Dahlem, Germany

[2] *Department of Synchrotron Radiation Research, Institute of Physics,*

Lund University, Box 118, SE-221 00 Lund, Sweden

[3] *National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

Abstract

Combining high-resolution core-level spectroscopy (HRCLS), scanning tunneling microscopy (STM) and density-functional theory (DFT) calculations we reanalyze the Pd(100)-($\sqrt{5} \times \sqrt{5}$)$R27^o$-O surface oxide phase. We find that the prevalent structural model, a rumpled PdO(001) film suggested by previous low energy electron diffraction (LEED) work (M. Saidy *et al.*, Surf. Sci. **494**, L799 (2001)), is incompatible with all three employed methods. Instead, we suggest the two-dimensional film to consist of a strained PdO(101) layer on top of Pd(100). LEED intensity calculations show that this model is compatible with the experimental data of Saidy *et al.*

(submitted to Surf. Sci.)

Contact person: Mira Todorova (todorova@fhi-berlin.mpg.de)

Al(111)- $(\sqrt{3} \times \sqrt{3})R30$: Rb,K - on-top vs substitutional adsorption

P. Scharoch

Wroclaw University of Technology, Wyb. Wyspianskiego 27,
50-370 Wroclaw, Poland

J. Neugebauer, M. Scheffler

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

Abstract

The atomic structure and energetics of the on-top and substitutional phase of the Al(111)-$(\sqrt{3} \times \sqrt{3})R30$:Rb adsorbate system have been studied employing density-functional theory total-energy calculations. Since the energy difference between the two phases is extremely small ($\approx 20\,meV$) extensive checks with respect to the choice of the exchange-correlation functional (LDA and GGA) and the construction of the Rb pseudopotential have been performed. All tests clearly show the substitutional adsorption site to be energetically favorable. Equivalent calculations performed for K revealed a clear chemical trend in the adsorption energetics for Na, K and Rb: The energy gain between the substitutional and the on-top configuration decreases with increasing atomic radius of an alkali atom. The calculated equilibrium geometries are in good agreement with previously reported experimental data.

Surface structure and adatom kinetics of group-III nitrides.

J. Neugebauer

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

Abstract

Recent results based on density-functional theory calculations concerning the structure and stability of GaN surfaces are discussed. An analysis of the thermodynamically stable surface structures for this materials system reveals that the driving mechanisms behind surface reconstructions are fundamentally different to those in "traditional" (i.e. arsenic or phosphorus based) III-V semiconductors. Specifically, surfaces are always metal-rich and nitrogen atoms on and in the surface layer are thermodynamically unstable. This feature will be shown to have important consequences on surface morphology, adatom kinetics, growth, reactivity, and alloy formation.

Walter Kohn – Personal Stories and Anecdotes Told by Friends and Collaborators

Cover Text

This is not a science book, nor even a book about science, although most of the contributors are scientists. It is a book of personal stories about Walter Kohn, a theoretical physicist and winner of half of the 1998 Nobel Prize in Chemistry. Walter Kohn originated and/or refined a number of very important theoretical approaches and concepts in solid-state physics. He is known in particular for Density-Functional Theory. This book represents a kind of "oral history" about him, gathered - in anticipation of his 80th birthday - from former students, collaborators, fellow-scientists, and friends.

Molecular adsorption on the surface of transition-metal oxides: Effects of strong electronic correlations

A. Rohrbach, J. Hafner, and G. Kresse

Institut für Materialphysik and

Center for Computational Material Science, Universität Wien,

Sensengasse 8/12, A-1090 Wien, Austria

Abstract

It is well-known that the physical properties of some transition-metal compounds (mostly oxides) are strongly affected by intra-atomic correlations. Very recently, investigations of the adsorption of small molecules such as CO on the surfaces of transition-metal oxides have led to rather surprising results: the weak adsorbate-substrate bonding and the asymmetric (tilted) adsorption geometries contrast sharply the strong bonding and symmetric geometries characteristic for metallic surfaces. Calculations based on either Hartree-Fock or density-functional methods have failed to explain these observations. For bulk transition-metal oxides it has been demonstrated that the addition of a Hubbard-type on-site Coulomb repulsion U to the local-density Hamiltonian (DFT+U) leads to an improved description of the electronic structure of these materials, but a consistent description of all physical properties proved to be elusive. In the present work, we present a comprehensive investigation of bulk NiO and of clean and CO-covered NiO(100) surfaces. We demonstrate that adding the on-site Coulomb-repulsion to the spin-polarized gradient-corrected density-functional Hamiltonian (SGGA+U) leads to a consistently improved description of a wide range of cohesive, electronic and magnetic properties of NiO (bulk and surface) and a very accurate description of the adsorption properties of CO. The effects of the strong electronic correlations in the substrate on the adsorbate-substrate bonding are discussed in detail.

Electronic, structural and optical properties of conjugated polymers based on carbazole, fluorene and borafluorene

Jean-Francois Brière and Michel Côté

Département de physique et Groupe de recherche en physique et technologie des couches minces(GCM), Université de Montréal,

C. P. 6128 Succursale Centre-ville, Montréal (Québec) H3C 3J7, Canada

Abstract

We present an ab initio study of the structural, electronic and optical properties of four conjugated polymers: poly(para-phenylene)(PPP), poly(2,7-fluorene)(PF), poly(2,7-carbazole)(PC) and poly(2,7-borafluorene)(PBF), and of their isolated constituent molecules. All the calculations were done using density functional theory(DFT) with a plane-wave basis set, pseudopotentials and local exchange-correlation energy. Resemblances in the atomic structure of the systems studied allow us to make correspondence between their wave functions near the Fermi energy. The dihedral angles of the polymers under consideration are all similar, varying between 26 and 27 degrees. In agreement with experimental data, we find smaller energy gaps for carbazole and borafluorene, compared to biphenyl and fluorene, which is due to differences in the HOMO or LUMO wave functions. However, for the polymers, the experimental gap for PC was found to be almost the same as for PPP and PF. Our calculations explain this experimental observation which is attributed to a change in the ordering of the last two valence bands between carbazole and its polymer. We also find that the energy gap of PBF, which has not been synthesized yet, should be smaller then the minimum energy gaps of the other studied polymers by approximately 0.5 eV. The polarizations for the first electronic transitions are presented from the analysis of the wave functions' symmetries. We find excellent agreement between the calculated and available experimental data validating the predictions made.

Contact person: michel.cote@umontreal.ca

Calculations of hyperfine parameters in antimony compounds

A. Svane

Department of Physics and Astronomy, University of Aarhus,
DK-8000 Aarhus C, Denmark

Abstract

The electron contact density and electric field gradient on the Sb nuclear position is calculated in a series of 22 Sb compounds, comprising metallic, covalent as well as ionic Sb(III) and Sb(V) systems. The full-potential linear-muffin-tin-orbitals method is used with the local-density-approximation for exchange and correlation effects. By comparison with experimental ^{121}Sb and ^{123}Sb nuclear quadrupole resonance data and ^{121}Sb Mössbauer data, the calibration constants relating measured quadrupole coupling constants and isomer shifts to the electric field gradient and the electron contact density, respectively, are derived. This leads to an accurate determination of the quadrupole moment of the ^{121}Sb nuclear ground-state as $Q = (-66.9 \pm 1.5)$ fm^2. The difference between the mean square radius of the ^{121}Sb nucleus in its excited isomeric and ground states is found to be $\Delta <r^2> = -(0.0521 \pm 0.0015)$ fm^2,

Oxide formation at the surface of late 4*d* transition metals: Insights from *first-principles atomistic thermodynamics*

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

Abstract

Using density-functional theory we assess the stability of bulk and surface oxides of the late 4*d* transition metals in a "constrained equilibrium" with a gas phase formed of O$_2$ and CO. While the stability range of the most stable bulk oxide extends for ruthenium well into gas phase conditions representative of technological CO oxidation catalysis, this is progressively less so for the 4*d* metals to its right in the periodic system. Surface oxides could nevertheless still be stable under such conditions. These thermodynamic considerations are discussed in the light of recent experiments, emphasizing the role of (surface) oxides as the active phase of model catalysts formed from these metals.

Ab initio theory of exchange interactions in itinerant magnets

I. Turek[1], J. Kudrnovský[2], V. Drchal[2], P. Bruno[3], and S. Blügel[4]

[1] *Institute of Physics of Materials, ASCR, Brno, Czech Republic*
[2] *Institute of Physics, ASCR, Prague, Czech Republic*
[3] *Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany*
[4] *Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*

Abstract

The paper reviews an ab initio two-step procedure to determine thermodynamic properties of itinerant magnets. In the first step, the selfconsistent electronic structure of a system is calculated using the tight-binding linear muffin-tin orbital method combined with Green function techniques. In the second step, the parameters of the effective classical Heisenberg Hamiltonian are determined using the magnetic force theorem and they are employed in subsequent evaluation of magnon spectra, the spin-wave stiffness constants and the Curie/Néel temperatures. Applicability of the developed scheme is illustrated by investigations of selected properties of $3d$ metals Fe, Co, and Ni, diluted magnetic semiconductors (Ga,Mn)As, and $4f$ metals Gd and Eu.

Exchange interactions at surfaces of Fe, Co, and Gd

I. Turek[1], S. Blügel[2], G. Bihlmayer[2], and P. Weinberger[3]
[1] *Institute of Physics of Materials, ASCR, Brno, Czech Republic*
[2] *Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*
[3] *Center for Computational Materials Science, TU Vienna, Austria*

Abstract

Magnetic exchange interactions at low-index surfaces of bcc iron, hcp cobalt, and hcp gadolinium are studied using *ab initio* electronic structure calculations. Interlayer exchange couplings derived from total-energy differences are enhanced at the surfaces over their bulk counterparts. This trend is in contrast to a surface reduction of on-site exchange parameters formulated within a classical Heisenberg model. A particular attention is paid to the sensitivity of exchange interactions at a Gd(0001) surface to relaxation of interlayer distances. The calculated results do not provide support for recently observed surface enhancement of the Curie temperature of the Gd metal.

Ab initio theory of exchange interactions and the Curie temperature of bulk Gd

I. Turek[1], J. Kudrnovský[2], G. Bihlmayer[3], and S. Blügel[3]

[1] *Institute of Physics of Materials, ASCR, Brno, Czech Republic*
[2] *Institute of Physics, ASCR, Prague, Czech Republic*
[3] *Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*

Abstract

An *ab initio* approach to magnetic properties of bulk hexagonal Gd is developed that is based on the local spin-density approximation with the $4f$ electrons treated as localized core electrons. The effective one-electron problem is solved using the tight-binding linear muffin-tin orbital method in the atomic-sphere approximation with the valence basis consisting of s-, p-, and d-type orbitals. The approach leads to a correct description of ground-state properties like the stability of ferromagnetic structure, the magnetic moment and the equilibrium lattice constant. Application of a real-space Green-function formalism yields the exchange pair interactions between distant neighbours that are inevitable for quantitative studies of magnetic excitations. The distance dependence and anisotropy of the exchange pair interactions are presented and the Curie temperature in the mean-field approximation is evaluated. The obtained value of 334 K is in a much better agreement with the experimental value of 293 K than previous theoretical results. Depending on the atomic volume we find an unusually large dependence of the Curie temperature on the c/a ratio, which bears important consequences for the critical temperatures of thick strained Gd films as grown on various substrates.

11 Book Announcements

"Nanoelectronics and Information Technology - Advanced Electronic Materials and Novel Devices"

Publisher: Wiley-VCH
Full size/full color
approx. 1000 pages
EUR 74.90

It is my pleasure to bring to your attention this recently published book. It is a textbook primarily aimed at students of physics, electrical engineering and information technology, as well as material science in their 3rd year and above. It is equally of interest to professionals wanting a broader overview of this subject. Because it emphasizes the basic principles, the book will retain its value despite the rapid developments in this field.

The book is a non-profit making venture, e. g. all authors and the editor have agreed to forego their royalties, in order to keep the price within an acceptable range for students. If you like the scope, the samples pages, and - finally - the book itself, would you be kind enough to pass this information on to your students and colleagues.

With kind regards,

Rainer Waser

An Introduction to Maximally-Localized Wannier Functions

Nicola Marzari[1], Ivo Souza[2], and David Vanderbilt[2]

[1] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-8407*

[2] *Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854-8019*

Abstract

The electronic ground state of a periodic system is usually described in terms of extended Bloch orbitals, simultaneous eigenstates of the periodic Hamiltonian and of the direct lattice translations. An alternative representation in terms of localized orbitals has been introduced by Gregory Wannier in 1937; besides its theoretical relevance in several areas of solid-state theory, it has gained recent prominence due to its connection with the Berry-phase theory of bulk polarization, the interest in linear-scaling approaches, and with the development of general algorithms to derive Wannier functions in the framework of first-principles electronic structure calculations. The connection between the Bloch representation and the Wannier representation is realized by families of transformations in a continuous space of unitary matrices, carrying a large degree of arbitrariness. A few years ago we have developed a localization algorithm that allows one to iteratively transform the extended Bloch orbitals of a first-principles calculation into a unique set of *maximally-localized* Wannier functions (MLWFs), extending and encompassing Boys formulation for molecules to the solid-state case. The localization algorithm is independent of the single-particle electronic structure approach adopted, or the choice of basis set, and it is straightforwardly applied to extended or periodic solids and to isolated systems. Additionally, a novel disentanglement procedure allows to extract a maximally-connected manifold of any chosen dimension from a given energy window, leading to the extension of the original algorithm to the case of systems without gaps (e.g., metals) and removing the limitation to isolated groups of bands separated by gaps from higher and lower manifolds. In this Highlight we will outline and summarize the main results of the theory and algorithm underlying the maximally-localized Wannier-functions representation, and review some of the applications that have since appeared in the literature.

1 Introduction

The electronic ground state of a periodic solid, in the independent-particle approximation, is naturally labeled according to the prescriptions of Bloch's theorem: single-particle orbitals are assigned a quantum number $\mathbf{k}$ for the crystal momentum, together with a band index n. Although this choice is widely used in electronic structure calculations, alternative representations are available. The Wannier representation [1, 2, 3], essentially a real-space picture of localized orbitals, assigns as quantum numbers the lattice vector $\mathbf{R}$ of the cell where the orbital is localized, together with a band-like index n.

Wannier functions can be a powerful tool in the study of the electronic and dielectric properties of materials: they are the solid-state equivalent of "localized molecular orbitals" [4, 5, 6, 7], and thus provide an insightful picture of the nature of chemical bonding, otherwise missing from the Bloch picture of extended orbitals. By transforming the occupied electronic manifold into a set of maximally-localized Wannier functions (MLWFs), it becomes possible to obtain an enhanced understanding of chemical coordination and bonding properties via an analysis of factors such as changes in shape or symmetry of the MLWFs, or changes in the locations of their centers of charge. In particular, the charge center of a MLWF provides a kind of classical correspondence for the "location of an electron" (or electron pair) in a quantum-mechanical insulator, allowing for the definition of insightful pair-distribution functions between electrons and ions. This analogy is extended further by the modern theory of bulk polarization [8, 9], which directly relates the vector sum of the centers of the Wannier functions to the macroscopic polarization of a crystalline insulator. Thus, the heuristic identification by which the displacements of the Wannier centers provide a microscopic map of the local polarization field is augmented, via the theory of polarization, by an exact statement relating the sum of displacements to the exact quantum-mechanical polarization of the system. Beside the above points, which are of obvious physical and chemical interest, the MLWFs are now also being used as a very accurate minimal basis for a variety of algorithmic or theoretical developments, with recent applications ranging from linear-scaling approaches [10] to the construction of effective Hamiltonians for the study of ballistic transport [11], strongly-correlated electrons [12, 13, 14], self-interaction corrections, and photonic lattices [15, 16].

Wannier functions are strongly non-unique. This is a consequence of the phase indeterminacy $e^{i\phi_n(\mathbf{k})}$ that Bloch orbitals $\psi_{n\mathbf{k}}$ have at every wavevector $\mathbf{k}$. This indeterminacy is actually more general than just the phase factors; Bloch orbitals belonging to an isolated group of bands (i.e., a set of bands that are connected between themselves by degeneracies, but separated from others by energy gaps) can undergo arbitrary unitary transformations $U^{(\mathbf{k})}$ between themselves at every $\mathbf{k}$. We have recently developed a procedure [17] that can iteratively refine these otherwise arbitrary degrees of freedom, so that they lead to Wannier functions that are well defined and that are localized around their centers (in particular, they minimize the second moment around the centers). Such a procedure can be applied either to an entire band complex of Bloch orbitals, or just to some isolated subgroups.
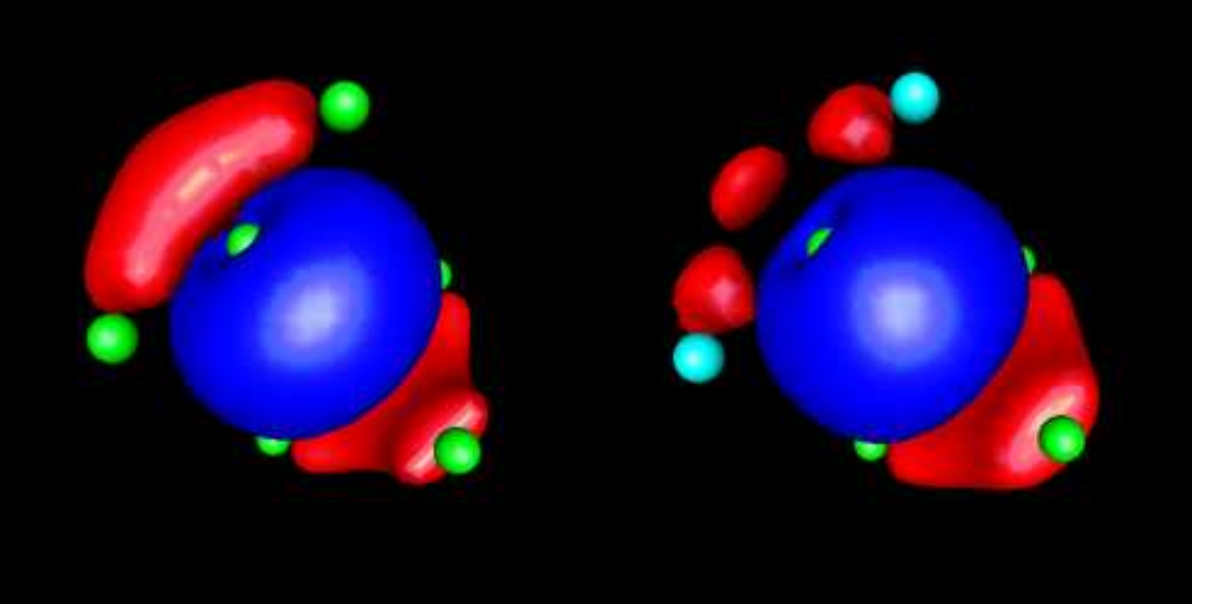
Figure 1: Amplitude isosurface contours for maximally-localized Wannier functions in Si (left panel) and GaAs (right panel). Red and blue contours are for isosurfaces of identical absolute value but opposite signs; Si and As atoms are in green, Ga in cyan. Each unit cell displays four (spin-unpolarized) equivalent WFs, localized around the centers of the four covalent bonds; breaking of inversion symmetry in GaAs polarizes the WFs towards the more electronegative As anion.

2   Method

Electronic structure calculations are often carried out using periodic boundary conditions. This is the most natural choice for the study of perfect crystals and for minimizing finite-size effects in the study of several non-periodic systems (e.g., surfaces or impurities). The one-particle effective Hamiltonian $\hat{H}$ then commutes with the lattice-translation operator $\hat{T}_{\mathbf{R}}$, allowing one to choose as common eigenstates the Bloch orbitals $|\psi_{n\mathbf{k}}\rangle$,

$$[\hat{H},\,\hat{T}_{\mathbf{R}}] \;=\; 0 \;\;\Rightarrow\;\; \psi_{n\mathbf{k}}(\mathbf{r}) \;=\; e^{i\phi_n(\mathbf{k})}\,u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}} \;\;, \tag{1}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ has the periodicity of the Hamiltonian. There is an arbitrary phase $\phi_n(\mathbf{k})$, periodic in reciprocal space, that is not assigned by the Schrödinger equation and that we have written out explicitly. We obtain a (non-unique) Wannier representation using any unitary transformation of the form $\langle\, n\mathbf{k}\,|\,\mathbf{R}n\,\rangle = e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}$:

$$|\,\mathbf{R}n\,\rangle \;=\; \frac{V}{(2\pi)^3}\int_{BZ} |\,\psi_{n\mathbf{k}}\,\rangle\,e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}\,d\mathbf{k} \;\;. \tag{2}$$

Here V is the real-space primitive cell volume, and $\varphi_n(\mathbf{k}+\mathbf{G}) = \varphi_n(\mathbf{k})$, for any reciprocal-lattice translation $\mathbf{G}$. It is easily shown that the $|\,\mathbf{R}n\,\rangle$ form an orthonormal set, and that two Wannier functions $|\,\mathbf{R}n\,\rangle$ and $|\,\mathbf{R}'n\,\rangle$ transform into each other with a translation of a lattice vector $\mathbf{R}-\mathbf{R}'$ [18]. The arbitrariness that is present in $\varphi_n(\mathbf{k})$ [or $\phi_n(\mathbf{k})$] propagates to the resulting Wannier functions, making the Wannier representation non-unique.

Since the electronic energy functional in an insulator is also invariant with respect to a unitary transformation of its N occupied Bloch orbitals, there is additional freedom associated with the choice of a full unitary matrix (and not just a diagonal one) transforming the orbitals between themselves at every wavevector $\mathbf{k}$. Thus, the most general operation that transforms the Bloch orbitals into Wannier functions is given by

$$| \mathbf{R}n \rangle \; = \; \frac{V}{(2\pi)^3} \int_{BZ} \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})} | \psi_{m\mathbf{k}} \rangle \, e^{-i\mathbf{k}\cdot\mathbf{R}} \, d\mathbf{k} \; , \tag{3}$$

where $U_{mn}^{(\mathbf{k})}$ is a unitary matrix of dimension N. Alternatively, we can regard this as a two-step process in which one first constructs Bloch-like orbitals

$$| \widetilde{\psi}_{n\mathbf{k}} \rangle = \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})} | \psi_{m\mathbf{k}} \rangle \tag{4}$$

and then constructs Wannier function $| w_n \rangle$ from the manifold of states $| \widetilde{\psi}_{n\mathbf{k}} \rangle$. The extra unitary mixing may be optional in the case of a set of discrete bands that do not touch anywhere in the Brillouin zone, but it is mandatory when describing a case like that of the four occupied bands of silicon, where there are degeneracies at symmetry points in the Brillouin zone. An attempt to construct a single Wannier function from the single lowest-energy or highest-energy band would be doomed in this case, because of non-analyticity of the Bloch functions in the neighborhood of the degeneracy points. Instead, the introduction of the unitary matrices $U_{mn}^{(\mathbf{k})}$ allows for the construction of states $| \widetilde{\psi}_{n\mathbf{k}} \rangle$ that are everywhere smooth functions of $\mathbf{k}$. In this case, the Wannier functions $w_n(\mathbf{r} - \mathbf{R}) = | \mathbf{R}n \rangle$, can be shown to be well localized: for a $\mathbf{R}_i$ far away from $\mathbf{R}$, $w_n(\mathbf{R}_i - \mathbf{R})$ is a combination of terms like $\int_{BZ} u_{m\mathbf{k}}(0)e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R})} \, d\mathbf{k}$, which are small due to the rapidly varying character of the exponential factor [18]. By way of illustration, the MLWFs that result from our procedure for the cases of Si and GaAs are shown in Fig. 1.

2.1 Maximally-localized Wannier functions

Several heuristic approaches have been developed that construct reasonable sets of Wannier functions, reducing the arbitrariness in the $U_{mn}^{(\mathbf{k})}$ with symmetry considerations and analyticity requirements [20, 21], or explicitly employing projection techniques on the occupied subspace spanned by the Bloch orbitals [22, 23] At variance with those approaches, we introduce a well-defined *localization criterion*, choosing the functional

$$\Omega = \sum_{n} \left[\langle \mathbf{0}n \, | \, r^2 \, | \, \mathbf{0}n \rangle \; - \; \langle \mathbf{0}n \, | \, \mathbf{r} \, | \, \mathbf{0}n \rangle^2 \right] \; = \; \sum_{n} \left[\langle r^2 \rangle_n - \bar{\mathbf{r}}_n^2 \right] \tag{5}$$

as the measure of the spread of the Wannier functions. The sum runs over the n functions $| \mathbf{0}n \rangle$; $\langle r^2 \rangle_n$ and $\bar{\mathbf{r}}_n = \langle \mathbf{r} \rangle_n$ are the expectation values $\langle \mathbf{0}n \, | \, r^2 \, | \, \mathbf{0}n \rangle$ and $\langle \mathbf{0}n \, | \, \mathbf{r} \, | \, \mathbf{0}n \rangle$. Given a set of Bloch orbitals $| \psi_{m\mathbf{k}} \rangle$, the goal is to find the choice of $U_{mn}^{(\mathbf{k})}$ in (3) that minimizes the values of the localization functional (5). We are able to express the gradient $G = \frac{d\Omega}{dW}$
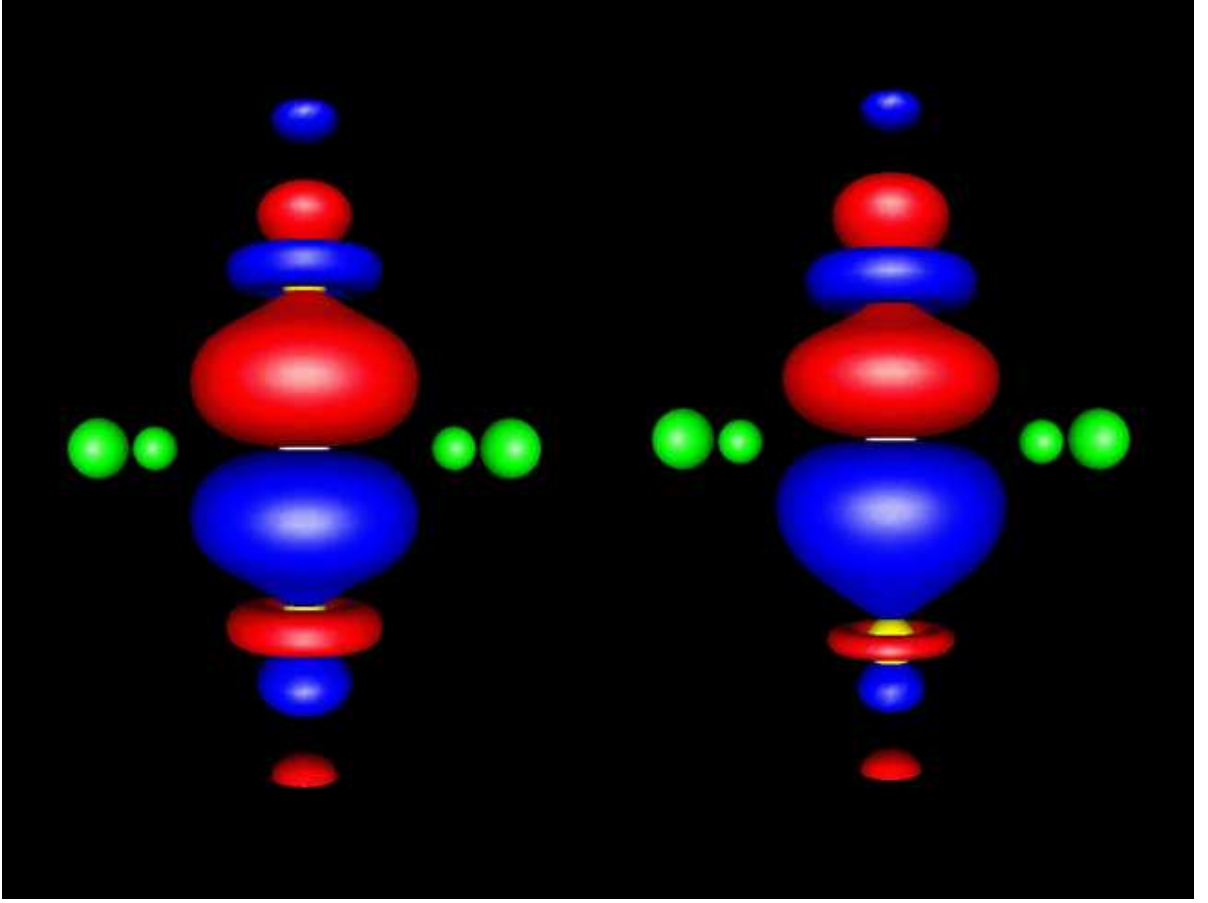
Figure 2: Isosurface contours for a maximally-localized Wannier function in BaTiO$_3$ in the paraelectric (left) and ferroelectric (right) phase. O atoms are in white, Ti yellow, and Ba green. The WF is one of the 9 originating from the composite group of the O 2p bands, showing strong and polarizable hybridization between the 2p_z orbital of O and the 3d_{z^2} orbitals of Ti, usually considered empty in an ionic picture. [From Ref. [19]]

of the localization functional with respect to an infinitesimal unitary rotation of our set of Bloch orbitals

$$|u_{n\mathbf{k}}\rangle \;\rightarrow\; |u_{n\mathbf{k}}\rangle + \sum_m dW_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle \;\;, \tag{6}$$

where dW an infinitesimal antiunitary matrix $dW^\dagger = -dW$ such that

$$U_{mn}^{(\mathbf{k})} = \delta_{mn} + dW_{mn}^{(\mathbf{k})} \;\;. \tag{7}$$

This provides an "equation of motion" for the evolution of the $U_{mn}^{(\mathbf{k})}$, and of the $|\mathbf{R}n\rangle$ derived in (3), towards the minimum of Ω; e.g., in the steepest-descent approach small finite steps in the direction opposite to the gradient decrease the value of Ω, until a minimum is reached. The unitary matrices are then used to construct the Wannier functions via Eq. (3), as illustrated for the semiconductors Si and GaAs in Fig. 1 and for the ferroelectric perovskite BaTiO$_3$ in Fig. 2.

133

2.1.1 Real-space representation

There are several interesting consequences stemming from the choice of (5) as the localization functional, that we briefly summarize here. Adding and subtracting the off-diagonal components $\widetilde{\Omega} = \sum_n \sum_{\mathbf{R}m \neq \mathbf{0}n} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2$, we obtain the decomposition

$$\Omega = \Omega_{\mathrm{I}} + \widetilde{\Omega} = \Omega_{\mathrm{I}} + \Omega_{\mathrm{D}} + \Omega_{\mathrm{OD}} \tag{8}$$

where Ω_{I}, $\widetilde{\Omega}$, Ω_{D} and Ω_{OD} are respectively

$$\Omega_{\mathrm{I}} = \sum_n \left[\langle \mathbf{0}n \, | \, r^2 \, | \, \mathbf{0}n \rangle - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2 \right] , \tag{9}$$

$$\widetilde{\Omega} = \sum_n \sum_{\mathbf{R}m \neq \mathbf{0}n} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2 ,$$

$$\Omega_{\mathrm{D}} = \sum_n \sum_{\mathbf{R} \neq \mathbf{0}} \left| \langle \mathbf{R}n | \mathbf{r} | \mathbf{0}n \rangle \right|^2 ,$$

$$\Omega_{\mathrm{OD}} = \sum_{m \neq n} \sum_{\mathbf{R}} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2 .$$

It can be shown that each of these quantities is *positive-definite* (in particular Ω_{I}, see Ref. [17]); moreover, Ω_{I} is also *gauge-invariant*, i.e., it is invariant under any arbitrary unitary transformation (3) of the Bloch orbitals. The minimization procedure thus corresponds to the minimization of $\widetilde{\Omega} = \Omega_{\mathrm{D}} + \Omega_{\mathrm{OD}}$. At the minimum, the elements $\left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2$ are as small as possible, realizing the best compromise in the simultaneous diagonalization, within the space of the Bloch bands considered, of the three position operators x, y and z (which do not in general commute when projected within this space).

2.1.2 Reciprocal-space representation

As shown by Blount [18], matrix elements of the position operator between Wannier functions take the form

$$\langle \mathbf{R}n | \mathbf{r} | \mathbf{0}m \rangle = i \frac{V}{(2\pi)^3} \int d\mathbf{k} \, e^{i\mathbf{k} \cdot \mathbf{R}} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{m\mathbf{k}} \rangle \tag{10}$$

and

$$\langle \mathbf{R}n | r^2 | \mathbf{0}m \rangle = -\frac{V}{(2\pi)^3} \int d\mathbf{k} \, e^{i\mathbf{k} \cdot \mathbf{R}} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}}^2 | u_{m\mathbf{k}} \rangle \ . \tag{11}$$

These expressions provide the needed connection with our underlying Bloch formalism, since they allow us to express the localization functional Ω in terms of the matrix elements of $\nabla_{\mathbf{k}}$ and $\nabla_{\mathbf{k}}^2$. In addition, they allow us to calculate the effects on the localization of any unitary transformation of the $|u_{n\mathbf{k}}\rangle$ without having to recalculate expensive (at least when plane-wave basis sets are used) scalar products. We thus determine the Bloch orbitals $|u_{m\mathbf{k}}\rangle$ on a regular mesh of $\mathbf{k}$-points, and will use finite differences to evaluate the above derivatives.

To proceed further, we make the assumption throughout this work that the Brillouin zone has been discretized into a uniform Monkhorst-Pack mesh, and the Bloch orbitals determined on that mesh.[1] Let $\mathbf{b}$ be a vector connecting a k-point to one of its near neighbors, and let Z be the number of such neighbors to be included in the finite-difference formulas. We use the simplest possible finite-difference formula for $\nabla_{\mathbf{k}}$, i.e., the one involving the smallest possible Z. When the Bravais lattice point group is cubic, it will only be necessary to include the first shell of $Z = 6$, 8, or 12 k-neighbors for simple cubic, bcc, or fcc k-space meshes, respectively. Otherwise, further shells must be included until it is possible to satisfy the condition

$$\sum_{\mathbf{b}} w_b\, b_\alpha b_\beta = \delta_{\alpha\beta} \tag{12}$$

by an appropriate choice of a weight w_b associated with each shell $|\mathbf{b}| = b$. (For the three kinds of cubic mesh, Eq. (12) is satisfied with $w_b = 3/Zb^2$ and a single shell of 6, 8, or 12 neighbors; even in the worst case of minimal symmetry, only six pairs of neighbors ($Z = 12$) are needed, as the freedom to choose six weights allows one to satisfy the six independent conditions comprising Eq. (12)). Now, if $f(\mathbf{k})$ is a smooth function of $\mathbf{k}$, its gradient can be expressed as

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_b\, \mathbf{b}\, [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})] \ . \tag{13}$$

In a similar way,

$$|\nabla f(\mathbf{k})|^2 = \sum_{\mathbf{b}} w_b\, [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})]^2 \ . \tag{14}$$

It now becomes straightforward to calculate the scalar products involving the reciprocal-space derivatives of Eqs. (10) and (11), since the only elements needed will be the matrix elements between Bloch orbitals at neighboring $\mathbf{k}$-points

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle \tag{15}$$

The $M_{mn}^{(\mathbf{k},\mathbf{b})}$ are a central quantity in our formalism, since we will express in their terms all the contributions to the localization functional. After some algebra [17] we can obtain the relevant quantities needed to compute the spread functional, that we report here starting from the center of nth orbital

$$\bar{\mathbf{r}}_n = -\frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b\, \mathbf{b}\, \mathrm{Im}\, \ln M_{nn}^{(\mathbf{k},\mathbf{b})} \ , \tag{16}$$

to its second moment

$$\langle r^2 \rangle_n = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b\, \left\{ \left[1 - |M_{nn}^{(\mathbf{k},\mathbf{b})}|^2\right] + \left[\mathrm{Im}\, \ln M_{nn}^{(\mathbf{k},\mathbf{b})}\right]^2 \right\} \tag{17}$$

---

[1] Even the case of Γ-sampling – where the Brillouin zone is sampled with a single $\mathbf{k}$-point – is encompassed by the above formulation. In this case the neighboring $\mathbf{k}$-points for Γ are given by the first shell(s) of reciprocal lattice vectors; the Bloch orbitals there differ only by phase factors $\exp(i\mathbf{G} \cdot \mathbf{r})$ from their counterparts at Γ. The algebra does become simpler, though, and will be discussed in a separate section.

and the different terms in the localization functional

$$\Omega_{\mathrm{I}} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \left(N_{\mathrm{bands}} - \sum_{mn} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2 \right), \tag{18}$$

$$\Omega_{\mathrm{OD}} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m \neq n} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2, \tag{19}$$

$$\Omega_{\mathrm{D}} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{n} \left(-\mathrm{Im}\, \ln M_{nn}^{(\mathbf{k},\mathbf{b})} - \mathbf{b} \cdot \bar{\mathbf{r}}_n \right)^2. \tag{20}$$

From these, we can calculate the change in the localization functional in response to an infinitesimal unitary transformation of the Bloch orbitals as a function of the $M_{mn}^{(\mathbf{k},\mathbf{b})}$; once these gradients are available, it is straightforward to construct a procedure that updates the $U_{mn}^{(\mathbf{k})}$ (and consequently the $M_{mn}^{(\mathbf{k},\mathbf{b})}$) towards the minimum localization.

3 Localization procedure

We now consider the first-order change of the spread functional Ω arising from an infinitesimal gauge transformation, given by $U_{mn}^{(\mathbf{k})} = \delta_{mn} + dW_{mn}^{(\mathbf{k})}$, where dW is an infinitesimal antiunitary matrix, $dW^\dagger = -dW$, so that $|u_{n\mathbf{k}}\rangle \rightarrow |u_{n\mathbf{k}}\rangle + \sum_m dW_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle$. We seek an expression for $d\Omega/dW_{mn}^{(\mathbf{k})}$. We use the convention

$$\left(\frac{d\Omega}{dW} \right)_{nm} = \frac{d\Omega}{dW_{mn}} \tag{21}$$

(note the reversal of indeces) and introduce $\mathcal{A}$ and $\mathcal{S}$ as the superoperators $\mathcal{A}[B] = (B - B^\dagger)/2$ and $\mathcal{S}[B] = (B + B^\dagger)/2i$. Defining

$$q_n^{(\mathbf{k},\mathbf{b})} = \mathrm{Im}\, \ln M_{nn}^{(\mathbf{k},\mathbf{b})} + \mathbf{b} \cdot \bar{\mathbf{r}}_n \tag{22}$$

$$R_{mn}^{(\mathbf{k},\mathbf{b})} = M_{mn}^{(\mathbf{k},\mathbf{b})} M_{nn}^{(\mathbf{k},\mathbf{b})*} \;\; ; \;\; \widetilde{R}_{mn}^{(\mathbf{k},\mathbf{b})} = \frac{M_{mn}^{(\mathbf{k},\mathbf{b})}}{M_{nn}^{(\mathbf{k},\mathbf{b})}} \;\; ; \;\; T_{mn}^{(\mathbf{k},\mathbf{b})} = \widetilde{R}_{mn}^{(\mathbf{k},\mathbf{b})} q_n^{(\mathbf{k},\mathbf{b})} . \tag{23}$$

and referring to Ref. [17] for the details, we arrive at the explicit expression for the gradient of the spread functional

$$G^{(\mathbf{k})} = \frac{d\Omega}{dW^{(\mathbf{k})}} = 4 \sum_{\mathbf{b}} w_b \left(\mathcal{A}[R^{(\mathbf{k},\mathbf{b})}] - \mathcal{S}[T^{(\mathbf{k},\mathbf{b})}] \right) . \tag{24}$$

In order to minimize the spread functional Ω by steepest descents, we make small updates to the unitary matrices, as in Eq. (7), choosing

$$dW^{(\mathbf{k})} = \epsilon\, G^{(\mathbf{k})}$$

where ϵ is a positive infinitesimal. We then have, to first order in ϵ,

$$d\Omega = \sum_{\mathbf{k}} \mathrm{tr}\,[G^{(\mathbf{k})} dW^{(\mathbf{k})}] = -\epsilon \sum_{\mathbf{k}} \|G^{(\mathbf{k})}\|^2 \ , \tag{25}$$

In practice, we take a fixed finite step $\Delta W^{(\mathbf{k})}$, and the wavefunctions are then updated according to the matrix $\exp[\Delta W^{(\mathbf{k})}]$, which is unitary since ΔW is antihermitian. The matrix $\exp[\Delta W^{(\mathbf{k})}]$ can be straightforwardly constructed from the eigenvalues and eigenvectors of $i\Delta W^{(\mathbf{k})}$, that is a regular Hermitian matrix.[2] More efficient minimization strategies should be used when dealing with large systems or very fine k-point meshes (e.g., conjugate-gradients minimizations).

It should be stressed that the evolution towards the minimum requires only the relatively inexpensive updating of the unitary matrices, and not of the wavefunctions. We start from a reference set of Bloch orbitals $|u_{n\mathbf{k}}^{(0)}\rangle$ obtained in our first-principles calculation, and compute once and for all the

$$M_{mn}^{(0)(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}}^{(0)}|u_{n,\mathbf{k}+\mathbf{b}}^{(0)}\rangle \ . \tag{26}$$

We then represent the $|u_{n\mathbf{k}}\rangle$ (and thus, indirectly, the Wannier functions) in terms of the $|u_{n\mathbf{k}}^{(0)}\rangle$ and a set of unitary matrices $U_{mn}^{(\mathbf{k})}$,

$$|u_{n\mathbf{k}}\rangle = \sum_{m} U_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}^{(0)}\rangle \ . \tag{27}$$

We begin with all the $U_{mn}^{(\mathbf{k})}$ initialized to δ_{mn}. Then, each step of the steepest-descent procedure involves calculating ΔW for a small step in the direction opposite to the gradient, updating the unitary matrices according to

$$U^{(\mathbf{k})} \ \rightarrow \ U^{(\mathbf{k})} \exp[\Delta W^{(\mathbf{K})}] \ , \tag{28}$$

and then computing a new set of M matrices according to

$$M^{(\mathbf{k},\mathbf{b})} = U^{(\mathbf{k})\dagger} M^{(0)(\mathbf{k},\mathbf{b})} U^{(\mathbf{k}+\mathbf{b})} \ . \tag{29}$$

In the most general case, the localization functional can display artificial "unphysical" local minima; to avoid these, we typically prepare a set of reference Bloch orbitals $|u_{n\mathbf{k}}^{(0)}\rangle$ by projection from a set of initial trial orbitals $g_n(\mathbf{r})$ corresponding to some very rough initial guess $g_n(\mathbf{r})$ for the Wannier functions. The $g_n(\mathbf{r})$ are projected onto the Bloch manifold at wavevector $\mathbf{k}$,

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m} |\psi_{m\mathbf{k}}\rangle\langle\psi_{m\mathbf{k}}|g_n\rangle \ , \tag{30}$$

are orthonormalized via the Löwdin transformation

$$|\widetilde{\phi}_{n\mathbf{k}}\rangle = \sum_{m} (S^{-1/2})_{mn}|\phi_{m\mathbf{k}}\rangle \tag{31}$$

---

[2] The unitary matrix $\exp(W)$ is obtained diagonalizing $H = iW$: since W is anti-Hermitian, H is Hermitian and has real eigenvalues ϵ_l and eigenvectors Z_{mn} such that $\epsilon_l = \sum_{mn} Z_{lm} H_{mn} Z_{nl}^{\dagger}$; then $(\exp(W))_{lm}$ is given by $\sum_n Z_{ln}^{\dagger} \exp(-i\epsilon_n) Z_{nm}$.

(where $S_{mn} = \langle \phi_{m\mathbf{k}} | \phi_{n\mathbf{k}} \rangle$), and finally reconverted to cell-periodic functions with

$$u_{n\mathbf{k}}^{(0)}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} \widetilde{\phi}_{n\mathbf{k}}(\mathbf{r}) \ . \tag{32}$$

We then use this set of reference Bloch orbitals as a starting point for the minimization procedure.

4   Two limiting cases: Isolated systems and large supercells

The formulation introduced above can be significantly simplified in two important cases, which merit a separate discussion. (i) When open boundary conditions are used instead of periodic boundary conditions; this is appropriate for treating finite, isolated systems (e.g., molecules and clusters) using localized basis sets, and is the standard approach in quantum chemistry. In this case the localization procedure can be entirely recast in real space, and corresponds to determining Boys localized orbitals of quantum chemistry. (ii) When the system studied can be described using a large periodic supercell. This is the case of amorphous solids or liquids; finite systems can also be described in this way, using large enough supercells so as to eliminate the interactions with periodic images. The Brillouin zone of a large supercell is sufficiently small that integrations over $\mathbf{k}$-vectors can be substituted with single-point sampling at its center (the Γ point).

4.1   Real-space formulation

We describe first the real-space localization procedure, changing notation $|\mathbf{R}n\rangle \rightarrow |w_i\rangle$ to refer to the orbitals of the isolated system that will become maximally localized. We decompose again the localization functional $\Omega = \sum_i [\langle r^2 \rangle_i - \bar{\mathbf{r}}_i^2]$ into an invariant part $\Omega_{\mathrm{I}} = \sum_\alpha \mathrm{tr}\,[P r_\alpha Q r_\alpha]$ (where $P = \sum_i |w_i\rangle\langle w_i|$, $Q = \mathbf{1} - P$, and 'tr' refers to a sum over all the states w_i) and a remainder $\widetilde{\Omega} = \sum_\alpha \sum_{i \neq j} |\langle w_i | r_\alpha | w_j \rangle|^2$ that needs to be minimized. Defining the matrices $X_{ij} = \langle w_i | x | w_j \rangle$, $X_{\mathrm{D},ij} = X_{ij}\,\delta_{ij}$, $X' = X - X_{\mathrm{D}}$, and similarly for Y and Z, $\widetilde{\Omega}$ can be rewritten as

$$\widetilde{\Omega} = \mathrm{tr}\,[X'^2 + Y'^2 + Z'^2] \ . \tag{33}$$

If X, Y, and Z could be simultaneously diagonalized, then $\widetilde{\Omega}$ could be minimized to zero (leaving only the invariant part); for non-commuting matrices this is not generally possible (although one could choose, as in [24], a preferred direction of localization). Our task is then to perform the optimal approximate simultaneous co-diagonalization of the three Hermitian matrices X, Y, and Z by a single unitary transformation. Although a formal solution for this problem is missing, implementing a numerical minimization (e.g., by steepest-descents or conjugate-gradient, see below) is fairly straightforward. This problem appears also in the context of multivariate analysis [25] and signal processing [26], and has been recently revisited in relation with the present localization approach [27] (see also Sec. IIIA in Ref. [28]). Since $\mathrm{tr}\,[X'X_{\mathrm{D}}] = 0$, etc.,

$$d\Omega = 2\,\mathrm{tr}\,[X'dX + Y'dY + Z'dZ] \ . \tag{34}$$

We then consider an infinitesimal unitary transformation $|w_i\rangle \rightarrow |w_i\rangle + \sum_j W_{ji}|w_j\rangle$ (where dW is antihermitian), from which $dX = [X, dW]$, etc. Inserting in Eq. (34) and using $\mathrm{tr}\,[A[B,C]] = \mathrm{tr}\,[C[A,B]]$ and $[X',X] = [X',X_\mathrm{D}]$, we obtain $d\Omega = \mathrm{tr}\,[dW\,G]$ where

$$G = 2\left\{[X', X_\mathrm{D}] + [Y', Y_\mathrm{D}] + [Z', Z_\mathrm{D}]\right\} \;, \tag{35}$$

so that the desired gradient is $d\Omega/dW = G$ as given above. The minimization can then be carried out using the general approach already outlined.

4.2   Γ-point formulation

With an appropriate redefinition of the quantities X_{ij}, a similar formulation applies in reciprocal space when dealing with isolated or very large systems in periodic boundary conditions, i.e., whenever it becomes appropriate to sample the wavefunctions only at the Γ-point of the Brillouin zone.

We start with the simpler case for a calculation in a cubic supercell of side L, following the derivation of Ref. [29]. The maximum-localization criterion turns out to be equivalent (see Eq. (41) below) to the problem of maximizing the functional

$$\Xi = \sum_{n=1}^{N} \left(|X_{nn}|^2 + |Y_{nn}|^2 + |Z_{nn}|^2\right) \;, \tag{36}$$

where $X_{mn} = \langle w_m|e^{-i\frac{2\pi}{L}x}|w_n\rangle$ (similar definitions for Y_{mn} and Z_{mn} apply). Once the gradient of this functional is determined, its maximization can be performed using again a steepest-descent algorithm.[3] Some simple algebra shows that the gradient $d\Xi/dA_{mn}$ is given by the sum of $[X_{nm}(X_{nn}^* - X_{mm}^*) - X_{mn}^*(X_{mm} - X_{nn})]$ and the equivalent terms with Y and Z substituted in place of X. We this start the procedure by constructing new matrices $X^{(1)}$, $Y^{(1)}$ and $Z^{(1)}$ via the unitary transformations $X^{(1)} = \exp(-A^{(1)})X^{(0)}\exp(A^{(1)})$ (and similarly for $Y^{(1)}$ and $Z^{(1)}$), where $X_{mn}^{(0)} = \langle w_m^{(0)}|e^{-i\frac{2\pi}{L}x}|w_n^{(0)}\rangle$ and $w_n^{(0)}(\mathbf{r}) = \psi_n(\mathbf{r})$ are the Kohn-Sham (KS) orbitals obtained after a conventional electronic structure calculation. $A^{(1)}$ is an $\mathbf{N} \times \mathbf{N}$ antihermitian matrix corresponding to a finite step in the direction of the gradient of Ξ with respect to all the possible unitary transformations given by $\exp(-A)$: $A^{(1)} = \lambda\,(d\Xi/dA)^{(0)}$, where λ is the length of the steepest-descent step. This process is repeated up to convergence in the Ξ functional – as always, more sophisticated algorithms can be used (e.g., introducing line searches along λ, or conjugate-gradient strategies). At the end of the iterative procedure, the maximally-localized Wannier functions are then given by the unitary rotation

$$w_n(\mathbf{r}) = \sum_m \left[\Pi_i \exp(-A^{(i)})\right]_{mn} \psi_m(\mathbf{r}) \tag{37}$$

---

[3]Note that in the limit of a single k point the distinction between Bloch orbitals and Wannier functions becomes irrelevant, since no Fourier transform from $\mathbf{k}$ to $\mathbf{R}$ is involved in the transformation (37); rather, we want to find the optimal unitary matrix that rotates the ground-state self-consistent orbitals into their maximally-localized representation.

of the original N orbitals. The coordinate x_n of the n-th Wannier-function center (WFC) is computed using the formula

$$x_n = -\frac{L}{2\pi} \, \text{Im} \, \ln \langle w_n | e^{-i\frac{2\pi}{L}x} | w_n \rangle \, , \tag{38}$$

with similar definitions for y_n and z_n. Eq. (38) has been shown by Resta to be the correct definition of the expectation value of the position operator for a system with periodic boundary conditions, and had been introduced several years ago to deal with the problem of determining the average position of a single electronic orbital in a periodic supercell [30]. The computational effort required in Eqs. (36) and (38) is negligible, once the scalar products needed to construct the initial $X^{(0)}$, $Y^{(0)}$ and $Z^{(0)}$ have been calculated.

The extension to supercells of arbitrary symmetry has been derived by Silvestrelli [31]. By defining overlap matrices

$$M^l_{mn} = \langle w_m | e^{-i\mathbf{G}_l \cdot \mathbf{r}} | w_n \rangle, \tag{39}$$

(where $\mathbf{G}_l$ are the reciprocal lattice vectors of the unit cell, w_j is the Wannier functions), a functional Ξ is defined as

$$\Xi = \sum_{n=1}^{N} \sum_{l=1}^{N_G} W_l \, |M^l_{nn}|^2 \tag{40}$$

(N_G is the number of the $\mathbf{G}_l$ vectors used, and W_l is the weight corresponding to the vector G_l). This functional is closely related to the spread of the Wannier functions:

$$
\begin{aligned}
\Omega &= \left(\frac{L}{2\pi}\right)^2 \sum_{n=1}^{N} \sum_{l=1}^{N_G} W_l \, [\, \langle w_n | (\mathbf{G}_l \cdot \mathbf{r})^2 | w_n \rangle - \langle w_n | \mathbf{G}_l \cdot \mathbf{r} | w_n \rangle^2 \,] \\
&= \left(\frac{L}{2\pi}\right)^2 \sum_{n=1}^{N} \sum_{l=1}^{N_G} W_l \, (1 - |\langle w_n | e^{-i\mathbf{G}_l \cdot \mathbf{r}} | w_n \rangle|^2 \,) + O(L^{-2}) \\
&= \left(\frac{L}{2\pi}\right)^2 \left(\sum_{n=1}^{N} \sum_{l=1}^{N_G} W_l - \Xi \right) + O(L^{-2}) \, , \tag{41}
\end{aligned}
$$

where L is the supercell dimension. Thus, instead of minimizing the spread, we maximize the functional Ξ to retrieve the MLWFs. The Wannier function center of the n'th occupied band, $\mathbf{r}_n$, can be computed from

$$\mathbf{r}_n = -\left(\frac{L}{2\pi}\right)^2 \sum_l W_l \, \mathbf{G}_l \, \text{Im} \, \ln M^l_{nn}. \tag{42}$$

Care should be taken when comparing the spreads of MLWFs calculated in supercells of different sizes. Even for the ideal case of an isolated molecule, the Wannier centers and the general shape of the MLWFs will rapidly reach their exact limit as the cell size is increased. On the other hand, the numerical value for the total spread Ω will display much slower convergence. This behavior derives from the finite-difference representation of the invariant part of the localization functional (essentially, it's a second derivative); while Ω_I

does not contribute to the localization properties of the MLWFs, it does numerically add up in the evaluation of the spreads, and usually represents the largest term. This slow convergence had already been noted in the original work [17] when commenting on the convergence properties of Ω with respect to the spacing of the Monkhorst-Pack mesh.

5   Entangled bands

In the case of bulk materials, the methods described in the previous sections were designed with *isolated* groups of bands in mind. By this we mean a group of bands that may become degenerate with one another at certain symmetry points or lines in the Brillouin zone (composite bands), but are separated from all other bands by finite gaps throughout the entire Brillouin zone (in the case of disordered systems it is more appropriate to think in terms of a gap in the density of states). The valence bands of insulators are the most important example, and indeed these methods have been applied mostly to insulating materials. However, in some applications the bands of interest are not isolated. This is the case when studying electron transport in metals, which is governed by the partially filled bands close to the Fermi level. The four low-lying antibonding bands of a tetrahedral semiconductor, which are connected to higher conduction bands, provide another example. In both cases the desired bands lie within a limited energy range but cross with, or are attached to, other bands which extend further out in energy. We will refer to them as *entangled* bands.

The difficulty in treating entangled bands stems from the fact that it is unclear exactly which N bands to choose, particularly in those regions of k space where the bands of interest are hybridized with unwanted bands. Before the Wannier-localization methods can be applied, some prescription is needed to extract N states per k point from the entangled manifold.

We have recently developed a strategy [32] that achieves this goal with minimal user intervention. Once an N-dimensional manifold has been obtained at each k, the usual localization procedure, based on minimizing $\widetilde{\Omega}$, can be used to generate the maximally-localized Wannier functions for that manifold. The problem of computing well-localized Wannier functions starting from entangled bands is then broken down into two distinct steps. The new feature is the first step (disentangling of the bands, or subspace selection), which is outlined below, while the second step is the same as for isolated groups of bands.

5.1   The disentangling procedure

5.1.1   Method

For definiteness let us suppose we want to disentangle the five d bands of copper from the s band which crosses them (see Fig. 3) and construct a set of well-localized WFs associated with the resulting d bands. Heuristically the d bands are the five narrow bands
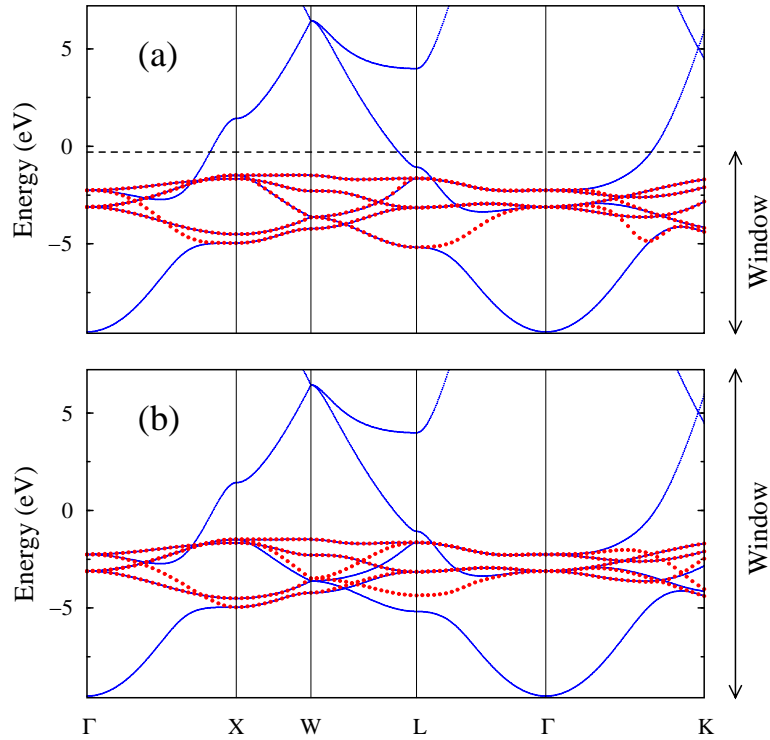
Figure 3: Blue lines: Calculated band structure of copper. Red lines: Interpolated bands obtained from the five d-like Wannier functions. (a) and (b) differ in the choice of energy window used in the disentangling step. [From Ref. [32]]

and the s band is the wide band. The difficulty arises because there are regions of k-space where all six bands are close together, so that as a result of hybridization the distinction between d-band and s-band levels is not meaningful.

First we cut out an energy window that encompasses the N bands of interest ($N = 5$ in our example). Figs. 3(a) and 3(b) correspond to different choices for this energy window. At each k-point the number $N_{\mathbf{k}}$ of bands that fall inside the window is equal to or larger than the target number of bands N. This procedure defines an $N_{\mathbf{k}}$-dimensional projective Hilbert space $\mathcal{F}(\mathbf{k})$ spanned by the eigenstates $|u_{n\mathbf{k}}\rangle$ within the window at some $\mathbf{k}$. If $N_{\mathbf{k}} = N$, there is nothing to do there; if $N_{\mathbf{k}}\rangle N$ our aim is to find the N-dimensional subspace $\mathcal{S}(\mathbf{k}) \subseteq \mathcal{F}(\mathbf{k})$ that, among all possible N-dimensional subspaces of $\mathcal{F}(\mathbf{k})$, leads to the smallest Ω_{I} [Eq. (18)]. Recall that for an isolated group of bands Ω_{I} is gauge-invariant, since it is an intrinsic property of the manifold of states. Thus Ω_{I} can be regarded as a functional of $\mathcal{S}(\mathbf{k})$. In practice $\mathcal{S}(\mathbf{k})$ is specified by an orthonormal set of N *pseudo*-Bloch states $|\widetilde{u}_{n\mathbf{k}}\rangle$, so that $\Omega_{\mathrm{I}} = \Omega_{\mathrm{I}}(\{\widetilde{u}_{n\mathbf{k}}\})$. We will then apply the procedure of Sec. 3 to the manifold of states $\mathcal{S}(\mathbf{k})$ in order to obtain a set of MLWFs spanning this space (see Fig. 4 for the MLWFs resulting from the disentangled d bands of copper).
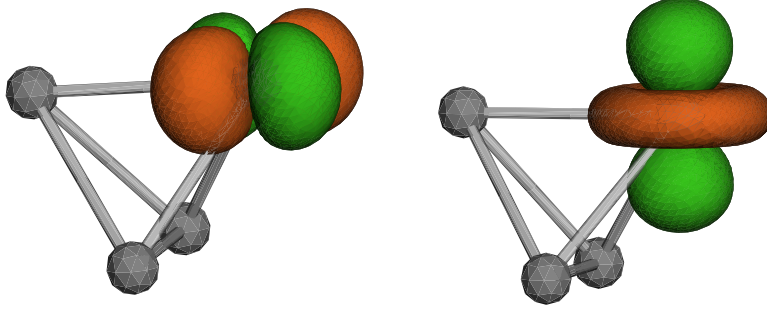
Figure 4: Contour-surface plots of the two e_g Wannier functions associated with the disentangled d bands of copper shown in Fig. 3. The amplitudes are $+0.5/\sqrt{v}$ (green) and $-0.5/\sqrt{v}$ (orange), where v is the volume of the primitive cell. [From Ref. [32]]

5.1.2 Rationale

Why is minimizing $\Omega_{\mathrm{I}}(\{\widetilde{u}_{n\mathbf{k}}\})$ a sensible strategy for picking out the d-bands? This can be understood by noting that Ω_{I} heuristically measures the change of character of the states across the Brillouin zone. Indeed, Eq. (18) shows that Ω_{I} is small whenever $|\langle \widetilde{u}_{n\mathbf{k}} | \widetilde{u}_{m,\mathbf{k}+\mathbf{b}}\rangle|^2$, the square of the magnitude of the overlap between states at nearby k-points, is large. Thus by minimizing Ω_{I} we are choosing self-consistently at every $\mathbf{k}$ the subspace $\mathcal{S}(\mathbf{k})$ that changes as little as possible with $\mathbf{k}$, i.e., has minimum "spillage" or mismatch with neighboring subspaces. In the present example this maximal "global smoothness of connection" will be achieved by keeping the five well-localized d-like states and excluding the more delocalized s-like state. This can be understood from the fact that Ω_{I} is a measure of real-space localization, a property that correlates with smoothness in k space.

What is meant by spillage becomes clear once we rewrite Eq. (18) for $\Omega_{\mathrm{I}}(\{\widetilde{u}_{n\mathbf{k}}\})$ as

$$\Omega_{\mathrm{I}} = \frac{1}{N_{\mathrm{kp}}} \sum_{\mathbf{k},\mathbf{b}} w_b \, T_{\mathbf{k},\mathbf{b}} \tag{43}$$

with

$$T_{\mathbf{k},\mathbf{b}} = \mathrm{tr}[\hat{P}_{\mathbf{k}} \, \hat{Q}_{\mathbf{k}+\mathbf{b}}], \tag{44}$$

where $\hat{P}_{\mathbf{k}} = \sum_n |\widetilde{u}_{n\mathbf{k}}\rangle \langle \widetilde{u}_{n\mathbf{k}}|$ is the projector onto $\mathcal{S}(\mathbf{k})$, $\hat{Q}_{\mathbf{k}} = \mathbf{1} - \hat{P}_{\mathbf{k}}$, and the indeces m, n run over $1, \ldots, N$. $T_{\mathbf{k},\mathbf{b}}$ is called the spillage between the spaces $\mathcal{S}(\mathbf{k})$ and $\mathcal{S}(\mathbf{k}+\mathbf{b})$ because it measures the degree of mismatch between them, vanishing when they are identical.

5.1.3 Numerical algorithm

The minimization of Ω_{I} inside an energy window is conveniently done using an algebraic algorithm. The stationarity condition $\delta\Omega_{\mathrm{I}}(\{\widetilde{u}_{n\mathbf{k}}\}) = 0$, subject to orthonormality

constraints, is equivalent to solving the set of eigenvalue equations

$$\left[\sum_{\mathbf{b}} w_b \hat{P}_{\mathbf{k+b}} \right] |\widetilde{u}_{n\mathbf{k}}\rangle = \lambda_{n\mathbf{k}} |\widetilde{u}_{n\mathbf{k}}\rangle . \tag{45}$$

Clearly these equations, one for each k point, are coupled, so that the problem has to be solved self-consistently throughout the Brillouin zone. Our strategy is to proceed iteratively until the maximal "global smoothness of connection" is achieved. On the i-th iteration we go through all the k-points in the grid, and for each of them we find N orthonormal states $\left|\widetilde{u}_{n\mathbf{k}}^{(i)}\right\rangle$, defining a subspace $\mathcal{S}^{(i)}(\mathbf{k}) \subseteq \mathcal{F}(\mathbf{k})$ such that the spillage over the neighboring subspaces $\mathcal{S}^{(i-1)}(\mathbf{k+b})$ from the previous iteration is as small as possible. In this iterative formulation one solves at each step the set of equations

$$\left[\sum_{\mathbf{b}} w_b \hat{P}_{\mathbf{k+b}}^{(i-1)} \right] \left|\widetilde{u}_{n\mathbf{k}}^{(i)}\right\rangle = \lambda_{n\mathbf{k}}^{(i)} \left|\widetilde{u}_{n\mathbf{k}}^{(i)}\right\rangle . \tag{46}$$

When constructing $\mathcal{S}^{(i)}(\mathbf{k})$ one should pick the N eigenvectors of Eq. (45) with largest eigenvalues, since that choice ensures that at self-consistency the stationary point corresponds to the absolute minimum of Ω_{I}. Self-consistency is achieved when $\mathcal{S}^{(i)}(\mathbf{k}) = \mathcal{S}^{(i-1)}(\mathbf{k})$ at all the grid points. We have encountered cases where the iterative procedure outlined above was not stable. In those cases, the problem was solved by using as the input for each step a linear mixing of the input and output subspaces from the previous step.

In practice we solve Eq. (46) in the basis of the original $N_{\mathbf{k}}$ Bloch eigenstates $|u_{n\mathbf{k}}\rangle$ inside the energy window. Each iteration then amounts to diagonalizing the following $N_{\mathbf{k}} \times N_{\mathbf{k}}$ Hermitian matrix at every $\mathbf{k}$:

$$Z_{mn}^{(i)}(\mathbf{k}) = \left\langle u_{m\mathbf{k}}\right| \sum_{\mathbf{b}} w_b \left[\hat{P}_{\mathbf{k+b}}^{(i-1)}\right]_{\mathrm{in}} \left|u_{n\mathbf{k}}\right\rangle. \tag{47}$$

Since these are small matrices, each step of the iterative procedure is computationally inexpensive. The most time-consuming part of the algorithm is the computation of the overlap matrices $M^{(\mathbf{k,b})}$. We stress that all $M^{(\mathbf{k,b})}$ are computed once and for all at the beginning of the Wannier postprocessing, using the original Bloch eigenstates inside the energy window [Eq. (26)]; all subsequent operations in the iterative minimization of Ω_{I} involve only dense linear algebra on small $N_{\mathbf{k}} \times N_{\mathbf{k}}$ matrices. (An analogous situation occurs during the minimization of $\widetilde{\Omega}$ to obtain the MLWFs: see Eqs. (28)-(29).)

As indicated above, having selected the maximally-connected N-dimensional subspaces $\mathcal{S}(\mathbf{k})$, in a second step we work within those subspaces and minimize $\widetilde{\Omega}$ using the same algorithm as for isolated groups of bands. The end result is a set of N maximally-localized WFs and the corresponding N energy bands (red lines in Fig. 3), which are computed from the WFs using an interpolation scheme.

Since in each step we have separately minimized the two terms, Ω_{I} and $\widetilde{\Omega}$, comprising the total Wannier spread Ω, we can regard the resulting orbitals as the N most-localized Wannier functions that can be obtained using states inside the energy window. It should

be understood that the Bloch-like states $|\widetilde{u}_{n\mathbf{k}}\rangle$ spanning the optimal subspaces $\mathcal{S}(\mathbf{k})$ do not simply correspond, by unitary rotation, to a subset of the Bloch eigenstates inside the window. Accordingly, the associated N energy bands do not reproduce exactly any subset of the original bands throughout the Brillouin zone. The differences are more pronounced where hybridization with unwanted bands in the original band structure was the strongest. The disentangling procedure can be easily modified [32] so that inside a second ("inner") energy window the original Bloch states – and hence the original bands – are exactly reproduced. The result of such a procedure is illustrated in Fig. 5 for copper. The two-window technique has been applied recently to electromagnetic bands in photonic crystals [15].
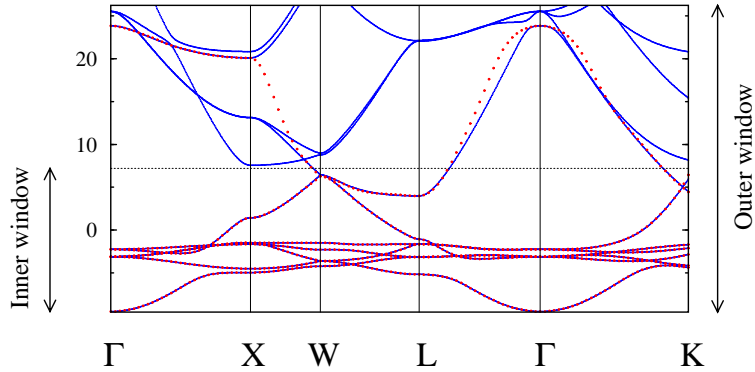
Figure 5: Blue lines: Calculated band structure of copper. Red lines: Interpolated bands for the maximally-connected seven-dimensional subspace using both an "outer" and an "inner" energy window. Inside the latter window the original and interpolated bands are identical. [From Ref. [32]]

6 Discussion

6.1 Alternative localization criteria

Even after the non-uniqueness of the Wannier functions is resolved (in our case by fixing all the gauge freedoms via the constraint of minimal quadratic spread), we are still left with an indeterminacy that follows from the existence of *different* plausible localization criteria. Other measures of localization have been used in the chemistry literature besides the most popular one of Boys [7]. For example, the Coulomb self-repulsion can be maximized, as in the Edmiston-Ruedenberg approach [33], or the projection on a Mulliken population, as in the Pipek-Mezey approach [34]. No matter which criterion is used, the vector sum of all Wannier centers over a primitive cell remains gauge-invariant, so that the connection to the macroscopic polarization is equally true for all localization criteria. However, the individual charge centers [35], the shapes, and even the symmetries of the Wannier functions may depend upon the choice of gauge (or of the choice of localization criterion that leads to the choice of gauge).

For isolated molecules, there is a slight theoretical preference for the Edmiston-Ruedenberg criterion, due to its ability to clearly separate σ- and π-like orbitals in double bonds. (The Boys criterion often mixes the two into so-called "banana" orbitals [34].) A well-known and most severe problem is the description of carbon dioxide (at least if the traditional O=C=O Lewis picture is upheld), where the Boys criterion leads to two triple bonds between the carbon and the oxygen, and one lone pair on each oxygen [36]. (We note in passing that this is actually reminiscent of CO_2 being a resonance structure between two states O≡C-O and O-C≡O.) On the other hand, the Boys criterion leads, in almost all other cases, to orbitals that are very similar to the Edmiston-Ruedenberg ones, and at a much reduced cost (cubic vs. quintic scaling with system size). It would be useful to carry out similar investigations comparing the use of different localization criteria in solids, but to our knowledge there have been no direct studies along these lines.

Nevertheless, we lean towards the view that in most cases the use of any "reasonable" localization criterion will lead to rather similar MLWFs that give a qualitatively and semiquantitatively similar description of the system of interest. The fact that the Boys and Edmiston-Ruedenberg MLWFs are usually so similar supports this viewpoint. Further support comes from the fact that we have seen very little difference in our results (especially when considering systems with high symmetry) when even simple projection techniques have been used [37, 12], along the lines of Eq. (30), without doing afterwards an actual minimization. For the case of silicon, localized orbitals very similar to our MLWFs have been obtained using a linear-scaling functional [38] that constrains the spread of an orbital inside a support region of finite (small) radius.

We report here the case case of high-pressure hydrogen, a molecular solid that shows significant infrared activity arising from overlap between the constituent molecules. In particular, we looked at the individual dipoles of the MLWFs in an attempt to extract from them useful physical information. An initial guess was made for the localized WFs with the help of trial functions which are bond-centered Gaussians (we will call the resulting orbitals "projected WFs"). Their localization was then refined by actually minimizing the quadratic spread Ω yielding the MLWFs. Since the projected WFs are totally oblivious to the localization criterion that one uses later to localize them further, it seems reasonable to assume that the difference between the projected and the MLWFs is an *upper bound* to the differences that would occur between WFs obtained using any two sensible localization criteria.

We show in Fig. 6 the results, for the solid in the $Cmc2_1$ structure at a density of $r_s = 1.52$, for which the average r.m.s. width of the MLWFs is $\overline{\lambda} = 1.11$ a.u. If we choose the r.m.s. width of the initial bond-centered Gaussians to be 1.89 a.u. (1 Å), the resulting projected WFs are essentially indistinguishable from the MLWFs. For instance, the curves corresponding to those in Fig. 6 are virtually identical, and the individual Wannier dipoles remain the same to at least six significant digits! This is compelling evidence for a high degree of uniqueness of well-localized WFs in this system, at least for our high-symmetry configurations. If we were to double the width of the initial Gaussian, some differences
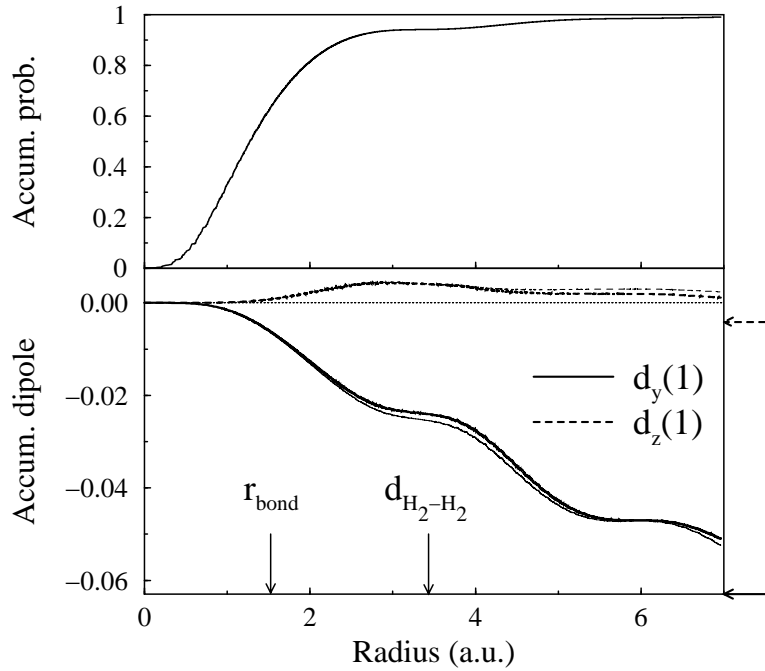
Figure 6: Upper panel: accumulated radial integral of the square of the MLWFs of an hydrogen molecule in the dense solid, $\int_{|\mathbf{r}|\langle r_0} |w_1(\mathbf{r})|^2 d\mathbf{r}$, as a function of r_0, for $Cmc2_1$ at $r_s = 1.52$; the integral starts at the molecular center and converges to one for large r_0. Lower panel, thick lines: accumulated radial integral of the Cartesian components of the Wannier dipole moment, $-2e \int_{|\mathbf{r}|\langle r_0} \mathbf{r}|w_1(\mathbf{r})|^2 d\mathbf{r}$ (the x-component vanishes by symmetry for all r_0); the arrows denote the converged values. The thin lines correspond to the WF obtained from bond-centered Gaussians with a r.m.s. width of 2.0 Å. [From Ref. [37]]

would start to appear. These are barely visible in the accumulated radial integral of the probability (see Fig. 6) but become noticeable, although still relatively small, in the radially integrated dipole (lower panel of Fig. 6). For instance, the large y-component of the dipole changes by around 2% (in $Cmc2_1$ the z-component is fixed by symmetry: $d_z(n) = v(P_{\mathrm{mac}})_z/2$, where $n = 1, 2$ labels the molecule in the primitive cell).

The dielectric decomposition of the charge density of an extended system into well-defined Wannier dipoles was first introduced for the case of liquid water by Silvestrelli and Parrinello [39]. Such analysis offers an enlightening picture of the electronic properties of a disordered system that wouldn't otherwise be available from the charge density alone, or from the eigenstates of the Hamiltonian. For the case of water a study was performed [40] spanning the phase diagram at intermediate steps between normal and supercritical conditions. Close to the low-density supercritical point there appears a shift in the average value for the Wannier dipoles, from a value around ~ 3 Debye under normal conditions (this is a typical value for liquid water [41]) to a much lower value close to the supercritical point, approaching the 1.86 Debye limit representing the dipole moment of an isolated molecule. This is a clear signature of the destabilization of the H-bond network, and the appearance of more and more water molecules with only weak interactions with their
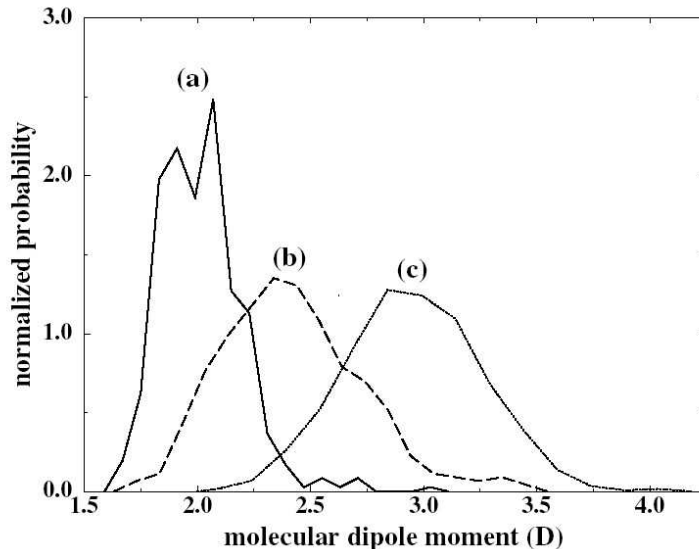
Figure 7: Distribution of the Wannier dipoles in supercritical water at a density of 0.32 g/cm^3 (a), and 0.73 g/cm^3 (b), compared with water at normal conditions (c).

neighbors (see Fig. 7).

It should be noted that the decomposition into Wannier dipoles is closer to the decomposition of the charge density into static (Szigeti) charges than to a decomposition into dynamical (Born) charges. The first one corresponds to a spatial decomposition of the total electronic charge density, while the second is connected with the force that appears on an atom in response to an applied electric field. Similarly, the Wannier dipoles provide a decomposition of the dielectric properties, maintaining the constraint that the total macroscopic polarization is correctly reproduced, but they do not describe the torque that would be exerted on the individual molecules by an electric field [42].

6.2 Open questions

There are several open questions that require further investigation, and represent intriguing directions towards a better formal understanding of the properties of the Wannier transformation.

We found that the MLWFs always turn out to be real in character, even if in the general case of a mesh of **k**-points different from Γ the Bloch orbitals themselves (and their periodic parts) will be complex. Even if this result seems plausible, we haven't been able to find or develop a proof for it (in the Γ-sampling formulation it becomes instead a trivial outcome, since the orbitals can always be chosen to be real to start with, propagating this characteristic across the minimization procedure).

Another related question has to do with the existence of concurrent minima for the localization functional in the space of the unitary matrices: we have found that in general there are multiple minima present (that's why we introduced a projection operation as

a starting condition in (30)), but that only when at the physically-meaningful absolute minimum the Wannier functions turn out to be real, while in all other cases they are intrinsically complex. This characteristic alleviates the problems related to minimizing a multiple-minima functional, since the absolute minimum always displays this characteristic reality (also, we find that once the projection operation is introduced, minimization always proceeds to the right minimum, even with very poor or random initial choices). We attribute the failure in finding the global minimum in complex cases, if projections are not used, to the complex and random phase relationship that can take place between orbitals in the 3d topology of the Brillouin zone. In the Γ-sampling formulation, on the other hand, we never observe convergence into a local minimum, and the functional appears well-behaved, with a single basin of attraction leading to the global minimum.

Finally, the asymptotic behavior of localized Wannier functions for the general 3-dimensional case is still an open question. While des Cloizeaux [43, 44] proved exponential localization for the projection operator for a three-dimensional manifold, a similar result for the individual Wannier functions is still missing. In the case of one-dimensional systems, on the other hand, exponential localization has been proven [2]; this result has also been recently extended to the determination of the algebraic prefactors modulating the exponential decay [45].

7   Applications

Several papers have appeared in the recent literature that make significant use of the MLWFs. We highlight some of these in here, without the pretense of being exhaustive or of encompassing all published results. Broadly speaking, most applications can be grouped into one of three main themes:

- A tool to understand the nature of the chemical bond.

- A descriptor of local and global dielectric properties.

- A basis set for linear-scaling approaches and for constructing model Hamiltionians.

7.1   The Nature of the Chemical Bond

Once the electronic ground state has been decomposed into well-localized orbitals, it becomes possible and meaningful to study the spatial distribution and the average properties of their centers of charge (the WFCs). Silvestrelli et al. argued [29] that the WFCs can be a powerful tool to understand bonding in low-symmetry cases, representing both an insightful and an economical mapping of the continuous electronic degrees of freedom into a set of classical descriptors (the position of the WFCs, and the spread of their MLWFs). The benefits of this approach become apparent when studying the properties of disordered systems (see Fig. 8 for an example of the MLWFs in the distorted tetrahedral network of amorphous silicon). In amorphous solids the analysis of the microscopic properties is
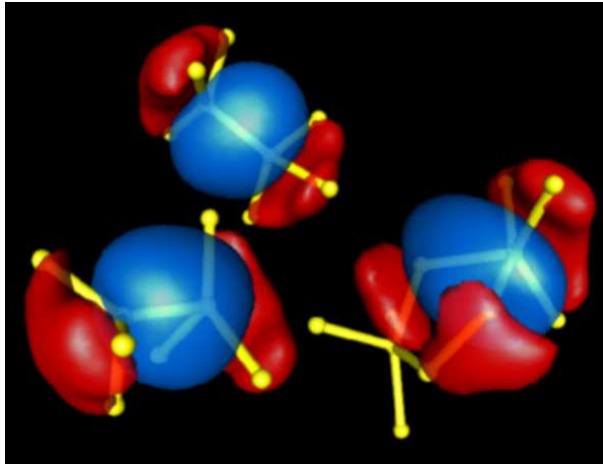
Figure 8: Maximally-localized Wannier functions in amorphous silicon, either around distorted but fourfold coordinated atoms, or in the presence of a fivefold defect. [From Ref. [46]]

usually based on the coordination number, i.e., on the number of atoms lying inside a sphere of a chosen radius r_c centered on the selected atom (r_c can be inferred with various degrees of confidence from the first minimum in the pair-correlation function). This purely geometrical analysis is completely blind to the actual electronic charge distribution, which ought to be important in any description of chemical bonding. An analysis of the full charge distribution and bonding in terms of the Wannier functions would be rather complex (albeit useful to characterize the most common defects [46]). Instead, just the knowledge of the positions of the WFCs and of their spreads can capture most of the chemistry in the system and can identify all the defects present. In this, the WFCs are treated as a second species of classical particles ("classical" electrons, represented by their centers), and the amorphous solid is treated as a statistical assembly of two kinds of particles, ions and WFCs.

We show in Fig. 9 the Si-Si $g(r)$ pair correlation function averaged over samples obtained with high-temperature first-principles molecular dynamics, and augment it with the plot of Si-WFC $g_w(r)$ pair correlation function. Both correlation functions display clear peaks (around $\simeq 2.4$ Åand $\simeq 1.2$ Å, respectively) and minima, showing that the electronic charge is mostly localized in the middle of the covalent bonds, as expected for amorphous silicon. Additional smaller peaks appear in the $g_w(r)$ correlation function for r around 0.5–1.0 Å (see inset); these peaks point to existence of a few anomalous MLWFs that are very close to a single Si atom. In order to make the analysis quantitative, we can calculate the usual coordination number (integrating the $g(r)$ up to its first minimum at $r_c = 2.80$ Å). We find that, on average, 96.5 % of the Si ions are fourfold coordinated, while 3.5 % are fivefold coordinated, in agreement with previous simulations [47]. We can now introduce our *novel bonding criterion*, based on the locations of the WFCs. The existence of a bond between two ions is defined by their sharing of a common WFC located within $r_w = 1.75$ Å of each ion (this is the position of the first minimum for the $g_w(r)$). Following this definition, we now find that 97.5 % of the Si ions are fourfold bonded; of the remaining
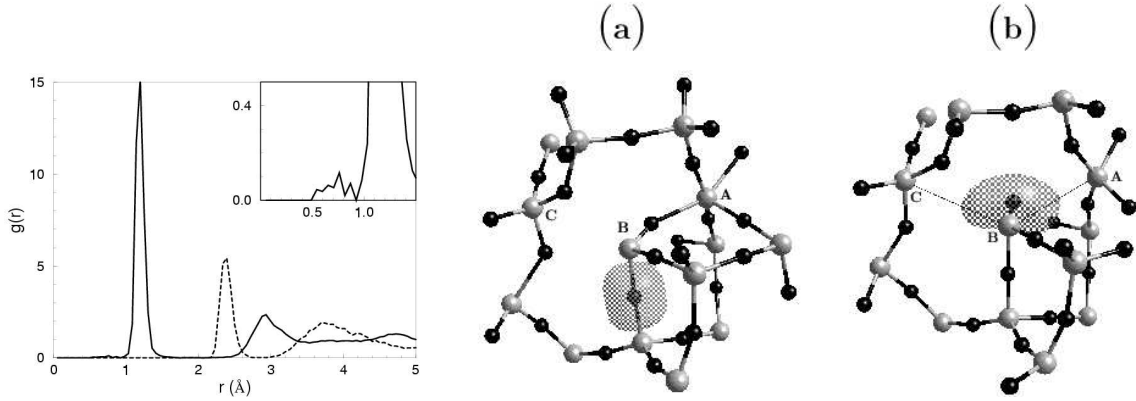
Figure 9: Left panel: Si-Si (dashed line) and Si-WFC (solid line) pair-correlation functions, from a 10 ps Car-Parrinello run on a 64-atom supercell. The detailed structure, in the range 0.0–1.5 Å, is shown in the inset. Right panel: Snapshots from 2 different timesteps in the simulation, corresponding to configurations where A and B maintain their coordination (5 and 4 respectively), but change their bonding (5→4 and 4→3 respectively). Small black "atoms" are the Wannier centers. [From Ref. [29]]

ions, only ~ 0.6 % have five bonds, while the others are more or less equally divided into twofold-bonded and threefold-bonded ions. The total density of defective atoms that we obtain is similar to that of the coordination analysis, but now the electronic signature of the defects emerges in a remarkably different way.

This fact is best illustrated by inspection of some selected configurations from the molecular-dynamics runs. We show in the middle and right panels of Fig. 9 two different configurations that have the same coordination environment (e.g. for the case of ions A and B). For the initial configuration in (a) we obtain from our bonding analysis that ion A, fivefold coordinated, has also five bonds, while ion B, fourfold coordinated, has only three bonds (e.g. no WFC is found between ion B and ion C). As the ions move (see Fig. 9(b)). the electronic configuration also changes, and after about 10 ps the WFC located between ion A and ion B gets even closer to ion B, at a distance of 0.57 Å, and in such a way that the A–B bond is broken or at least severely weakened. In this configuration, according to our criterion, ion A is fourfold bonded, while ion B has only *two* bonds; further inspection of the density profile of one of these "lone pair" MLWFs shows how it is clearly different from a regular covalent bond. In addition, the spread is considerably larger, providing a very simple criteria that makes electronic defects straightforwardly identifiable in a MLWFs analysis.

Besides its application to the study of disordered networks [49, 50, 51], the above analysis can also be effectively employed to elucidate the chemical and electronic properties accompanying structural transformations. In a recent work on silicon nanoclusters under pressure [52, 53, 48], the location of the WFCs was monitored during compressive loading (up to 35 GPa) and unloading (see Fig. 10). The analysis of the "bond angles"
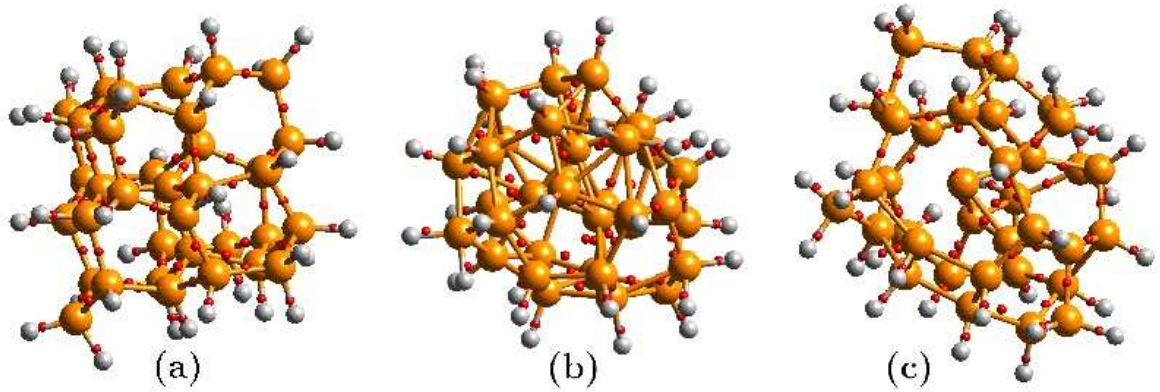
Figure 10: Collapse and amorphization of a Si cluster under pressure (increasing to 25 GPa (a), 35 GPa (b) and back to 5 GPa (c)). Small red "atoms" are the Wannier centers. [From Ref. [48]]

formed by two WFCs and their common silicon atom shows considerable departure from the tetrahedral rule at the transition pressure (Fig. 11). At the same pressure the ML-WFs become significantly more delocalized (inset of Fig. 11), hinting at a metallization transition similar to that happening for Si from the diamond structure into β-tin.

Interestingly, the MLWFs analysis can also point to structural defects that do not exhibit any significant electronic signature. Goedecker et al. [54] have recently predicted – entirely from first-principles – the existence of a new fourfold-coordinated defect that is stable inside the Si lattice (see Fig. 12). This defect had not been considered before, but displays by far the lowest formation energy – at the density-functional theory level – among all defects in silicon. Inspection of the relevant "defective" MLWFs reveals that their spreads remain actually very close to those typical of crystalline silicon, and that the WFCs remain equally shared between the atoms, in a very regular covalent arrangement. These considerations suggest that the electronic configuration is locally almost indistinguishable from that of the perfect lattice, making this defect difficult to detect with standard electronic probes. Also, a low activation energy is required for the self-annihilation of this defect; this consideration, in combination with the "stealth" electronic signature, hints at why such a defect could have eluded experimental discovery (if it does indeed exist !) despite the fact that Si is one of the best studied materials in the history of technology.

Moving towards more complex chemical systems, the MLWF analysis has been used in understanding and monitoring the nature of the bonding under varying thermodynamical conditions or along a chemical reaction in systems as diverse as ice [55], doped fullerenes [56], adsorbed organic molecules [57], ionic solids [58, 59] and in a study of the Ziegler-Natta polymerization [60]. This latter case (see Fig. 13) is a paradigmatic example of the chemical insight that can be gleaned following the WFCs in the course of an ab-initio simulation. In the Ziegler-Natta polymerization we have an interconversion of a double
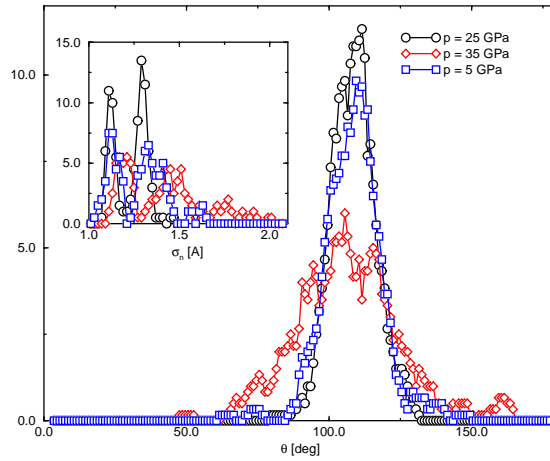
Figure 11: Distribution of the WFC-Si-WFC bond angles for the configurations shown in Fig. 10. The inset tracks in an histogram the spreads of the MLWFs at different pressures. [From Ref. [48]]
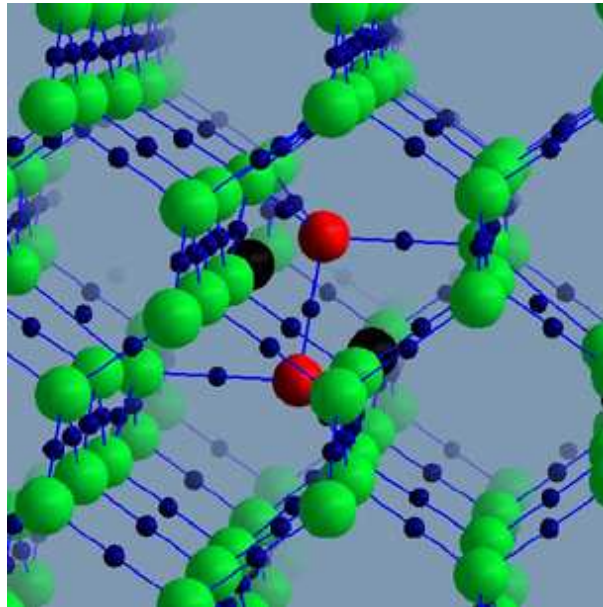

Figure 12: The recently-discovered fourfold coordinated defect in Si. Si atoms are in green, vacancies in black, and the centers of the MLWFs in blue, with a radius proportional to their spread. [From Ref. [54]]
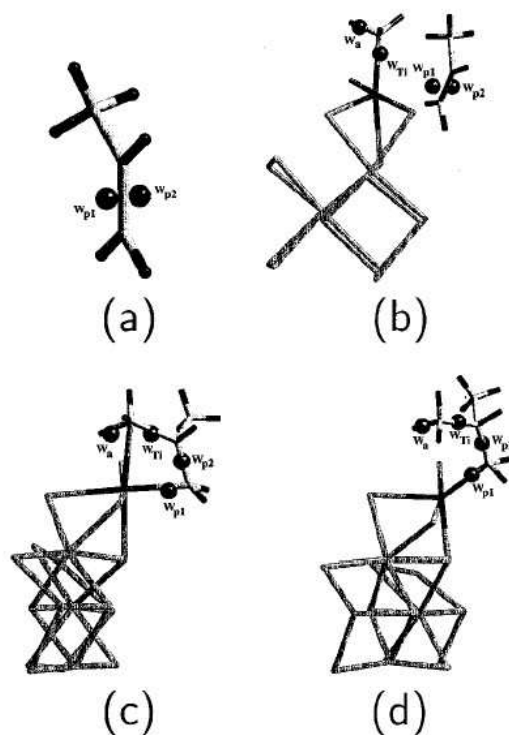
Figure 13: Propene polymerization at a Ti catalytic site on a $MgCl_2$ substrate. The evolution of the WFCs is shown, going from an isolated propene molecule (a) to the complexation with the catalyst (b) and to the formation of the polymeric chain (d) via the transition state (c). The breaking of the double carbon bond becomes clearly evident, as is the α-*agostic* interaction manifest in the displacement of one of the C-H centers in the methyl group. [From Ref. [60]]

carbon bond into a single bond, and a characteristic *agostic* interaction between the C-H bond and the activated metal center. Both become immediately visible once the WFCs are monitored, greatly aiding the interpretation of the complex chemical pathways.

As discussed before, the MLWF analysis has been pioneered by the group of M. Parrinello and applied initially to the study of the properties of liquid water. For example, we show in Fig. 14 (left panel) a snapshot from a molecular dynamics simulation, explicitly showing some of the dynamical connections along hydrogen bonds. The nature of the hydrogen bond becomes already explicit in the MLWFs for an isolated water dimer (center and right panels of Fig. 14), where the hybridization between orbitals in the two molecules is clearly visible. Applications of the Wannier-function technique to water have been numerous, from studies at normal conditions to high- and low-pressure phases at high temperature [39, 41, 40, 61, 62, 63]. Results from one of these simulations are shown in Fig. 15, during a fast dissociation events. The work on the structure of pure water has now been augmented by the study of the solvation and dielectric properties of ions in water [64, 65, 66, 67, 68]; recently even more complex biochemical systems have been investigated, ranging from wet DNA [69] to HIV-1 protease [70] or to phosphate groups in different environments (ATP, GTP and ribosomal units) [71, 72, 73, 74].
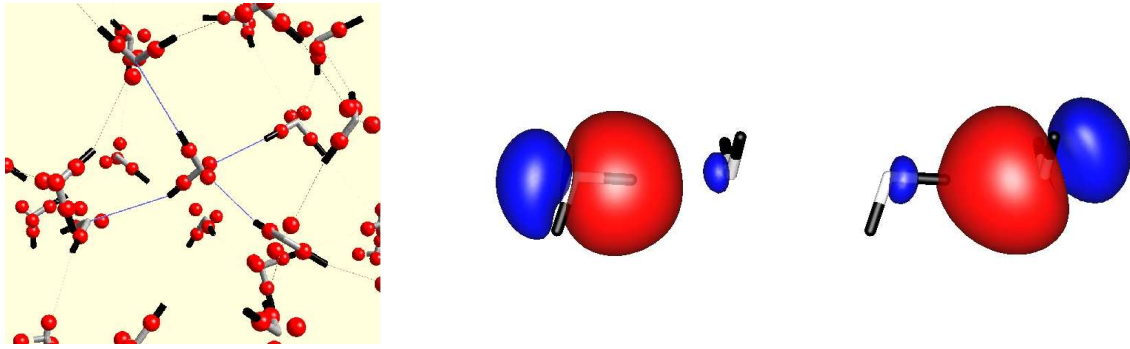
Figure 14: Left panel: WFCs (red) from a snapshot of a Car-Parrinello simulation of liquid water. The hydrogen atoms are in black and the oxygens in white; hydrogen bonds have also been highlighted. Center panel: MLWF for a O-H bond in a water dimer. Right panel: MLWF for a lone pair in a water dimer. [Left panel courtesy of P. L. Silvestrelli [41]]
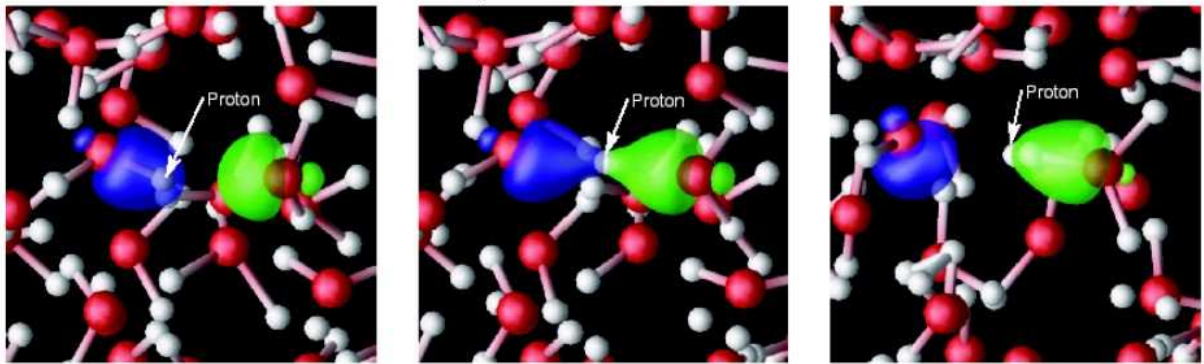

Figure 15: Snapshots of a rapid water-molecule dissociation under high-temperature (1390 K) and high-pressure (27 GPa) conditions; one of the MLWFs in the proton-donor molecule is highlighted in blue, and one of the MLWFs in the proton-acceptor molecule is highlighted in green. [From Ref. [62]]

Finally, localized orbitals can embody the chemical concept of transferable functional groups, and thus be used to construct a good approximation for the electronic-structure of complex systems starting for the orbitals for the different fragments [75].

7.2 Local and Global Dielectric Properties

The modern theory of polarization [8, 9] directly relates the vector sum of the centers of the Wannier functions to the polarization of an insulating system. This exact correspondence to a macroscopic observable (rigorously speaking, the change in polarization [76] upon a perturbation) cannot depend on the particular choice of representation: the sum of the Wannier centers is in fact invariant – as it should be – with respect to unitary transformations of the orbitals [35]. The existence of this exact relation between classical electrostatics and the quantum-mechanical WFCs suggests a heuristic identification by which the pattern of displacements of the WFCs can be regarded as defining a coarse-

grained representation for the polarization field $\mathbf{P}(\mathbf{r})$. This identification is reinforced by the insightful chemical description of the ground-state electronic structure that single MLWFs provide, as shown in the previous section.

A natural application of this formalism is directed towards the description of the Born dynamical (effective) charges. The Born dynamical charges describe the change in macroscopic polarization induced by the displacement of a given ion. As such, they play a fundamental role in determining the lattice-dynamical properties of insulating crystals (e.g., the intensity of infrared absorption), and are a powerful tool to investigate the dielectric and ferroelectric properties of materials. They also determine the splitting of the infrared-active optical modes; in simpler compounds (e.g. GaAs) they can be determined from the experimental zone-center phonons. Using the MLWF representation, it becomes possible not only to calculate the Born charges Z^* from the vector displacements of the sum of the WFCs induced by an ionic displacement, but also to naturally decompose them into contributions originating from individual MLWFs. As an example, we have studied GaAs in a cubic supercell in which one Ga atom has been displaced along the [111] direction. From the resulting displacement of the Wannier centers we derive a value for Z^*_{Ga} of 2.04, in good agreement with other theoretical predictions. Moreover, in arriving at the total electronic $Z^{*,\text{el}}_{\text{Ga}}=-0.96$, we find contributions of -1.91, $+0.65$, and $+0.30$ from the groups of four first-neighbor, twelve second-neighbor, and remaining further-neighbor Wannier centers, respectively. It is interesting to note that inclusion of nearest-neighbor contributions alone would significantly overestimate the magnitude of $Z^{*,\text{el}}_{\text{Ga}}$, and that the second-neighbor Wannier centers move in the opposite direction to the Ga atom motion. If we repeat the calculation displacing one As atom, we obtain a total Z^*_{As} of -2.07. The electronic $Z^{*,\text{el}}_{\text{As}}=-7.07$ has now contributions of -1.74, -4.63, and -0.71 from the four first-neighbors, twelve second-neighbor, and remaining further-neighbor Wannier centers, respectively.

Such decomposition is particularly instructive in the case of perovskite ferroelectrics, which often display anomalously large effective charges in comparison to their nominal ionic value [77, 78]. The origin of this effect lies in the large dynamical charge transfer that takes place when moving away from the high-symmetry cubic phase (i.e., going from more ionic to more covalent bonding). Orbital hybridization is necessary for this transfer to take place and our localized-orbitals approach provides an insightful tool in describing these effects. If the bonding were purely ionic, electrons (and thus Wannier centers) would be firmly localized on each anion, and move rigidly with it. This is not the case in perovskites, and the anomalous contribution is linked to substantial hybridization between the oxygen p orbitals and the d orbitals of the atom in the octahedral cage (see Fig. 2 for a pictorial description of this phenomenon). The picture can be even more complex, with other group of bands playing a role in the anomalous dielectric behavior, where again the MLWFs decomposition can measure the different contributions from separate groups of bands (equivalently available in a Bloch picture [79, 80, 81]), but also from specific atoms or bonds inside a composite group of bands [19].

Finally, Wannier functions are a particularly appropriate choice to study the effects of applied external fields on periodic or extended systems (periodic boundary conditions are in principle not compatible with constant applied fields). The localization properties of MLWFs have been directly exploited to calculate NMR chemical shifts [82]; also, even if not strictly necessary, MLWFs would allow for a straightforward implementation of recent proposals to describe the response to electric fields for periodic solids [83, 84].

7.3   MLWFs as a basis set: from linear-scaling to model Hamiltonians

One of the most attractive features calling for the use of localized orbitals in electronic-structure calculations is their ability to avoid computational bottlenecks deriving from non-local constraints. E.g., standard density-functional approaches suffer in the asymptotic limit from a cubic-scaling cost due to their orthonormality requirements. This factor of 8 can be easily identified by considering that if the size of a system studied is doubled, there will be twice as many orbitals to consider, each of them satisfying an orthonormality relation with twice as many orbitals, and with each overlap integrals having now a double cost (in order to keep the same resolution on a doubled integration domain). So, localization strategies are at the core of current efforts to develop truly linear-scaling approaches. For the case of orthonormality constraints, localized orbitals will only need to have those enforced with a small number of overlapping neighbors, and that number is generally independent of the system size.

A very promising implementation for a linear-scaling algorithm has been recently proposed in the context of (Diffusion) Quantum Monte Carlo calculations [10] and has already been applied to a variety of technologically-relevant nanoscale structures [85, 86]. In this formulation, the MLWFs representation is used to construct the Slater determinant for the trial wavefunction, at variance with the standard choice of single-electron eigenstates. The use of MLWFs makes the Slater determinant sparse, and with the additional benefits of introducing storage costs that are also linear-scaling. The benefits of this choice are immediately evident and shown in Fig. 16, with a plot for the cost of a single wavefunction evaluation as a function of the total number of electrons and for different choices for the basis set.

Besides this computational advantages, localized representations have long been used in theoretical condensed-matter theory to develop model Hamiltonians (e.g. Hubbard, t-J) able to capture the physics of strongly-correlated fermions. Some of these derivations are based on the Wannier picture, and recent works have taken the direct route of extracting the relevant interaction parameters from the MLWFs themselves [12, 13], with remarkable success in the description e.g. of the magnetic properties of cuprates. Similarly, MLWFs can be used to construct the Green's functions in the Landauer formulation of ballistic conductance [11], or to extend the formalism of correlated electrons to thermal transport properties [14].

Finally, less traditional approaches involve the construction of lattice Wannier functions
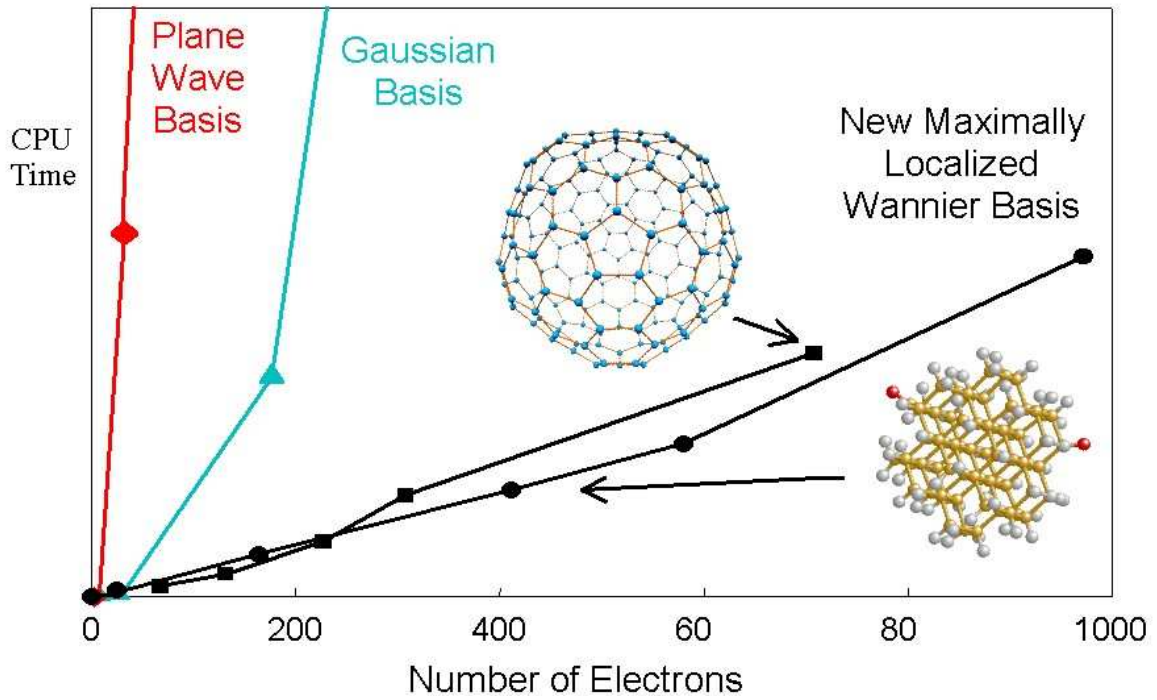
Figure 16: CPU time required to move a single configuration of electrons for one time step in silicon cluster and fullerenes, using a linear-scaling diffusion Monte Carlo approach that uses MLWFs as a basis set. [From Ref. [62]]

to model structural phase transitions in the solid-state [87, 88, 89], or, recently, photonic Wannier functions, with complete analogy between periodic electronic potentials and their Bloch or Wannier states, and periodic photonic lattices [90, 15, 16, 91].

7.4 Algorithmic Developments

We conclude by mentioning a number of algorithms and theoretical developments closely linked to the formulation presented in this work. These range from the extension of the MLWFs representation to the all-electron case [59], to the development of alternative minimization and localization algorithms [31, 28, 24, 92, 27], and to the many-body formulation of the position and localization operators [93, 94, 95, 96, 97].

8 Conclusions

We have described a theoretical and algorithmic framework for transforming the Bloch eigenfunctions into a localized Wannier representation. For a composite group of bands that is isolated (i.e., separated by gaps from other groups), optimal localization properties are obtained by minimizing a well-defined localization functional corresponding to the sum of the second moments of the orbitals around their centers of charge. The localization algorithm proceeds by iterating the degrees of freedom of the Wannier transformation,

158

i.e., a continuous set of unitary matrices defined everywhere in the Brillouin zone, with dimension equal to the number of bands to be transformed. This criterion is the extension to the solid state of the Boys localization criterion for isolated molecules, and reduces to it when dealing with large supercells containing isolated systems. The procedure has been extended to deal with entangled energy bands, i.e., to the case when the bands of interests are not separated by gaps from other bands. In this case, localization becomes a two-fold process. First we extract a maximally-connected subspace of chosen dimension from a given energy window, essentially requiring that the extracted manifold had minimal dispersion of its projection operator across the Brillouin zone. Second, we extract the maximally-localized Wannier functions from this well-connected subspace using our standard localization procedure. Lastly, we have shown how the localization algorithm simplifies considerably in the special case of Γ-point Brillouin-zone sampling appropriate for large supercells, and outlined the extension to the use of ultrasoft pseudopotentials for this case.

Applications of our approach are already numerous, and we have presented some of the early results available in the literature. Broadly speaking, there are three classes of applications where MLWFs have found natural use.

- The method is useful for the description of the chemical properties of complex systems, thanks to the intuitive connection between the MLWFs and the shape and symmetry of individual bonds, and the ability of MLWFs to summarize information about the electronic states in terms of their centers of charge.

- The dielectric properties of complex materials is well described in a local language. In particular, the macroscopic polarization is exactly related to the vector sum of the valence-band Wannier centers via the modern theory of polarization. Thus, local polarization properties can be heuristically represented by a field of Wannier dipoles, and thus, to the specific activity of well-defined atom- or bond-like MLWFs.

- MLWFs provide an efficient and accurate minimal basis set suitable for applications ranging from linear-scaling approaches, to the development of model Hamiltonians for strongly-correlated systems or for the electronic-transport properties, to applications outside the traditional realm of electronic-structure calculations (e.g., in the determination of lattice Wannier functions or photonic Wannier functions).

Further applications of this approach are envisioned, thanks to the ever-increasing availability of public electronic-structure software under the broad umbrella of the GNU Project / Free Software Foundation (see below), and its current incorporation in widely-used or distributed electronic-structure packages, such as the Car-Parrinello molecular-dynamics codes CPMD (IBM/MPI Stuttgart), JEEP (LLNL), and CP90 (Princeton University/EPFL Lausanne/University of Pisa/MIT).

9 Acknowledgments

10 Web site: www.wannier.org

The maximally-localized Wannier code for isolated, composite groups of bands is available under the GNU Public License at www.wannier.org, and can be interfaced to any electronic structure code able to calculate the scalar products $M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}}|u_{n,\mathbf{k}+\mathbf{b}}\rangle$. A public-domain version that includes the disentanglement procedure is also in progress.

Appendix: Extension to ultrasoft pseudopotentials

The extension of the localization formalism to the case of ultrasoft pseudopotentials *for the case of Γ-sampling only* is fairly straightforward and has been recently implemented (see Refs. [98, 99]). The formalism of Sec. 4.2 can be followed, where the appropriate scalar products M_{ij}^l introduced in (39) are now calculated via the augmentation operator $K(\mathbf{r})$, as defined in Ref. [100, 101]:

$$
\begin{aligned}
M_{mn}^l &= \langle w_m | K(\mathbf{r}) e^{-i\mathbf{G}_l\cdot\mathbf{r}} | w_n \rangle \\
&= \langle w_m(\mathbf{r}) | e^{-i\mathbf{G}_l\cdot\mathbf{r}} | w_n(\mathbf{r}) \rangle + \sum_{ij,I} \int Q_{ij}^I(\mathbf{r}) e^{-i\mathbf{G}_l\cdot\mathbf{r}} d\mathbf{r} \, \langle w_m | \beta_i^I \rangle \langle \beta_j^I | w_n \rangle .
\end{aligned} \tag{48}
$$

We foresee no particular difficulty in extending the ultrasoft MLWFs formalism to the case of general Monkhorst-Pack meshes, but we are not aware of any actual implementation to date.

References

[1] G. H. Wannier, "The structure of electronic excitation levels in insulating crystals," *Physical Review*, vol. 52, p. 191, 1937.

[2] W. Kohn, "Analytic properties of Bloch waves and Wannier functions," *Physical Review*, vol. 115, pp. 809–821, 1959.

[3] J. des Cloizeaux, "Orthogonal orbitals and generalized Wannier functions," *Physical Review*, vol. 129, no. 2, p. 554, 1963.

[4] S. F. Boys, "Construction of molecular orbitals to be approximately invariant for changes from one molecule to another," *Reviews of Modern Physics*, vol. 32, p. 296, 1960.

[5] J. M. Foster and S. F. Boys, "Canonical configurational interaction procedure," *Reviews of Modern Physics*, vol. 32, pp. 300–302, 1960.

[6] J. M. Foster and S. F. Boys, "A quantum variational calculation for HCHO," *Reviews of Modern Physics*, vol. 32, pp. 303–304, 1960.

[7] S. F. Boys, "Localized orbitals and localized adjustment functions," in *Quantum Theory of Atoms, Molecules, and the Solid State* (P.-O. Löwdin, ed.), pp. 253–262, New York: Academic Press, 1966.

[8] R. D. King-Smith and D. Vanderbilt, "Theory of polarization of crystalline solids," *Physical Review B*, vol. 47, no. 3, pp. 1651–1654, 1993.

[9] R. Resta, "Macroscopic polarization in crystalline dielectrics - the geometric phase approach," *Reviews of Modern Physics*, vol. 66, no. 3, pp. 899–915, 1994.

[10] A. J. Williamson, R. Q. Hood, and J. C. Grossman, "Linear-scaling quantum Monte Carlo calculations," *Physical Review Letters*, vol. 87, no. 24, p. 246406, 2001.

[11] A. Calzolari, N. Marzari, I. Souza, and M. Buongiorno Nardelli, "Ab-initio transport properties of nanostructures from maximally-localized Wannier functions," *in preparation*, 2003.

[12] W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, "Insulating ferromagnetism in La4Ba2Cu2O10: An ab initio Wannier function analysis," *Physical Review Letters*, vol. 89, no. 16, p. 167204, 2002.

[13] I. Schnell, G. Czycholl, and R. C. Albers, "Hubbard-U calculations for Cu from first-principle Wannier functions," *Physical Review B*, vol. 65, no. 7, p. 075103, 2002.

[14] I. Paul and G. Kotliar, "Thermal transport for many-body tight-binding models," *Physical Review B*, vol. 67, no. 11, p. 115131, 2003.

[15] D. M. Whittaker and M. P. Croucher, "Maximally localized Wannier functions for photonic lattices," *Physical Review B*, vol. 67, no. 8, p. 085204, 2003.

[16] A. Garcia-Martin, D. Hermann, F. Hagmann, K. Busch, and P. Wolfle, "Defect computations in photonic crystals: a solid state theoretical approach," *Nanotechnology*, vol. 14, no. 2, pp. 177–183, 2003.

[17] N. Marzari and D. Vanderbilt, "Maximally localized generalized Wannier functions for composite energy bands," *Physical Review B*, vol. 56, no. 20, pp. 12847–12865, 1997.

[18] E. I. Blount, "Formalisms of band theory," in *Solid State Physics* (F. Seitz and D. Turnbull, eds.), vol. 13, pp. 305–373, New York: Academic Press, 1962.

[19] N. Marzari and D. Vanderbilt, "Maximally-localized Wannier functions in perovskites: Cubic $BaTiO_3$," in *First-principles calculations for ferroelectrics* (R. E. Cohen, ed.), vol. 436, pp. 146–155, Woodbury NY: AIP Conference Proceedings, 1998.

[20] B. Sporkmann and H. Bross, "Calculation of Wannier functions for Fcc transition-metals by Fourier transformation of Bloch functions," *Physical Review B*, vol. 49, no. 16, pp. 10869–10876, 1994.

[21] B. Sporkmann and H. Bross, "Calculation of Wannier functions for zinc-blende-type semiconductors," *Journal of Physics-Condensed Matter*, vol. 9, no. 26, pp. 5593–5608, 1997.

[22] S. Satpathy and Z. Pawlowska, "Construction of bond-centered Wannier functions for silicon valence bands," *Physica Status Solidi B-Basic Research*, vol. 145, no. 2, pp. 555–565, 1988.

[23] U. Stephan, D. A. Drabold, and R. M. Martin, "Improved accuracy and acceleration of variational order-N electronic-structure computations by projection techniques," *Physical Review B*, vol. 58, no. 20, pp. 13472–13481, 1998.

[24] C. Sgiarovello, M. Peressi, and R. Resta, "Electron localization in the insulating state: Application to crystalline semiconductors," *Physical Review B*, vol. 64, no. 11, p. 115202, 2001.

[25] B. N. Flury and W. Gautschi, "An algorithm for the simultaneous orthogonal transformation of several positive definite symmetric matrices to nearly orthogonal form," *SIAM Journal on Scientific and Statistical Computing*, vol. 7, no. 1, pp. 169–184, 1986.

[26] J.-F. Cardoso and A. Souloumiac, "Jacobi angles for simultaneous diagonalization," *SIAM Journal on Matrix Analysis and Applications*, vol. 17, no. 1, pp. 161–164, 1996.

[27] F. Gygi, J.-L. Fattebert, and E. Schwegler, "Computation of maximally localized Wannier functions using a simultaneous diagonalization algorithm," *preprint*, vol. RL-JC-151591, pp. 1–12, 2003.

[28] G. Berghold, C. J. Mundy, A. H. Romero, J. Hutter, and M. Parrinello, "General and efficient algorithms for obtaining maximally localized Wannier functions," *Physical Review B*, vol. 61, no. 15, pp. 10040–10048, 2000.

[29] P. L. Silvestrelli, N. Marzari, D. Vanderbilt, and M. Parrinello, "Maximally-localized Wannier functions for disordered systems: Application to amorphous silicon," *Solid State Communications*, vol. 107, no. 1, pp. 7–11, 1998.

[30] A. Selloni, P. Carnevali, R. Car, and M. Parrinello, "Localization, hopping, and diffusion of electrons in molten- salts," *Physical Review Letters*, vol. 59, no. 7, pp. 823–826, 1987.

[31] P. L. Silvestrelli, "Maximally localized Wannier functions for simulations with supercells of general symmetry," *Physical Review B*, vol. 59, no. 15, pp. 9703–9706, 1999.

[32] I. Souza, N. Marzari, and D. Vanderbilt, "Maximally localized Wannier functions for entangled energy bands," *Physical Review B*, vol. 65, no. 3, p. 035109, 2002.

[33] C. Edmiston and K. Ruedenberg, "Localized atomic and molecular orbitals," *Reviews of Modern Physics*, vol. 35, pp. 457–465, 1963.

[34] J. Pipek and P. G. Mezey, "A fast intrinsic localization procedure applicable for ab-initio and semiempirical linear combination of atomic orbital wave-functions," *Journal of Chemical Physics*, vol. 90, no. 9, pp. 4916–4926, 1989.

[35] D. Vanderbilt and R. D. King-Smith, "Electric polarization as a bulk quantity and its relation to surface-charge," *Physical Review B*, vol. 48, no. 7, pp. 4442–4455, 1993.

[36] J. P. Foster and F. Weinhold, "Natural hybrid orbitals," *Journal of the American Chemical Society*, vol. 102, pp. 7211–7218, 1980.

[37] I. Souza, R. M. Martin, N. Marzari, X. Y. Zhao, and D. Vanderbilt, "Wannier-function description of the electronic polarization and infrared absorption of high-pressure hydrogen," *Physical Review B*, vol. 62, no. 23, pp. 15505–15520, 2000.

[38] P. Fernandez, A. DalCorso, A. Baldereschi, and F. Mauri, "First-principles Wannier functions of silicon and gallium arsenide," *Physical Review B*, vol. 55, no. 4, pp. R1909–R1913, 1997.

[39] P. L. Silvestrelli and M. Parrinello, "Water molecule dipole in the gas and in the liquid phase," *Physical Review Letters*, vol. 82, no. 16, pp. 3308–3311, 1999.

[40] M. Boero, K. Terakura, T. Ikeshoji, C. C. Liew, and M. Parrinello, "Hydrogen bonding and dipole moment of water at supercritical conditions: A first-principles molecular dynamics study," *Physical Review Letters*, vol. 85, no. 15, pp. 3245–3248, 2000.

[41] P. L. Silvestrelli and M. Parrinello, "Structural, electronic, and bonding properties of liquid water from first principles," *Journal of Chemical Physics*, vol. 111, no. 8, pp. 3572–3580, 1999.

[42] A. Pasquarello and R. Resta, "Dynamical monopoles and dipoles in a condensed molecular system: The case of liquid water," *in preparation*, 2003.

[43] J. D. des Cloizeaux, "Energy bands and projection operators in a crystal: Analytic and asymptotic properties," *Physical Review*, vol. 135, pp. A685–A697, 1964.

[44] J. D. des Cloizeaux, "Analytical properties of n-dimensional energy bands and Wannier functions," *Physical Review*, vol. 135, pp. A698–A707, 1964.

[45] L. X. He and D. Vanderbilt, "Exponential decay properties of Wannier functions and related quantities," *Physical Review Letters*, vol. 86, no. 23, pp. 5341–5344, 2001.

[46] M. Fornari, N. Marzari, M. Peressi, and A. Baldereschi, "Wannier functions characterization of floating bonds in a-Si," *Computational Materials Science*, vol. 20, no. 3-4, pp. 337–342, 2001.

[47] I. Stich, R. Car, and M. Parrinello, "Amorphous-silicon studied by ab-initio molecular-dynamics - preparation, structure, and properties," *Physical Review B*, vol. 44, no. 20, pp. 11092–11104, 1991.

[48] R. Martonak, C. Molteni, and M. Parrinello, "A new constant-pressure ab initio/classical molecular dynamics method: simulation of pressure-induced amorphization in a Si35H36 cluster," *Computational Materials Science*, vol. 20, no. 3-4, pp. 293–299, 2001.

[49] V. Meregalli and M. Parrinello, "An anomalous alloy: YxSi1-x," *Solid State Communications*, vol. 117, no. 7, pp. 441–444, 2001.

[50] S. H. N. Lim, D. G. McCullooch, A. R. Merchant, N. A. Marks, M. M. M. Bilek, and D. R. McKenzie, "Wannier function analysis for understanding disordered structures generated using Car-Parrinello molecular dynamics," *Molecular Simulation*, vol. 28, no. 10-11, pp. 971–979, 2002.

[51] P. Fitzhenry, M. M. M. Bilek, N. A. Marks, N. C. Cooper, and D. R. McKenzie, "Wannier function analysis of silicon-carbon alloys," *Journal of Physics-Condensed Matter*, vol. 15, no. 2, pp. 165–173, 2003.

[52] R. Martonak, C. Molteni, and M. Parrinello, "Ab initio molecular dynamics with a classical pressure reservoir: Simulation of pressure-induced amorphization in a Si35H36 cluster," *Physical Review Letters*, vol. 84, no. 4, pp. 682–685, 2000.

[53] C. Molteni, R. Martonak, and M. Parrinello, "First principles molecular dynamics simulations of pressure- induced structural transformations in silicon clusters," *Journal of Chemical Physics*, vol. 114, no. 12, pp. 5358–5365, 2001.

[54] S. Goedecker, T. Deutsch, and L. Billard, "A fourfold coordinated point defect in silicon," *Physical Review Letters*, vol. 88, no. 23, p. 235501, 2002.

[55] M. Bernasconi, P. L. Silvestrelli, and M. Parrinello, "Ab initio infrared absorption study of the hydrogen-bond symmetrization in ice," *Physical Review Letters*, vol. 81, no. 6, pp. 1235–1238, 1998.

[56] I. M. L. Billas, C. Massobrio, M. Boero, M. Parrinello, W. Branz, F. Tast, N. Malinowski, M. Heinebrodt, and T. P. Martin, "First principles calculations of Si doped fullerenes: Structural and electronic localization properties in C59Si and C58Si2," *Journal of Chemical Physics*, vol. 111, no. 15, pp. 6787–6796, 1999.

[57] P. L. Silvestrelli, F. Ancilotto, and F. Toigo, "Adsorption of benzene on Si(100) from first principles," *Physical Review B*, vol. 62, no. 3, pp. 1596–1599, 2000.

[58] L. Bernasconi, P. A. Madden, and M. Wilson, "Ionic to molecular transition in AlCl3: an examination of the electronic structure," *Physchemcomm*, vol. 5, no. 1, pp. 1–11, 2002.

[59] M. Posternak, A. Baldereschi, S. Massidda, and N. Marzari, "Maximally localized wannier functions in antiferromagnetic MnO within the FLAPW formalism," *Physical Review B*, vol. 65, no. 18, p. 184422, 2002.

[60] M. Boero, M. Parrinello, S. Huffer, and H. Weiss, "First-principles study of propene polymerization in Ziegler-Natta heterogeneous catalysis," *Journal of the American Chemical Society*, vol. 122, no. 3, pp. 501–509, 2000.

[61] M. Boero, K. Terakura, T. Ikeshoji, C. C. Liew, and M. Parrinello, "Water at supercritical conditions: A first principles study," *Journal of Chemical Physics*, vol. 115, no. 5, pp. 2219–2227, 2001.

[62] E. Schwegler, G. Galli, F. Gygi, and R. Q. Hood, "Dissociation of water under pressure," *Physical Review Letters*, vol. 87, no. 26, p. 265501, 2001.

[63] A. H. Romero, P. L. Silvestrelli, and M. Parrinello, "Compton scattering and the character of the hydrogen bond in ice I-h," *Journal of Chemical Physics*, vol. 115, no. 1, pp. 115–123, 2001.

[64] F. C. Lightstone, E. Schwegler, R. Q. Hood, F. Gygi, and G. Galli, "A first principles molecular dynamics simulation of the hydrated magnesium ion," *Chemical Physics Letters*, vol. 343, no. 5-6, pp. 549–555, 2001.

[65] E. Schwegler, G. Galli, and F. Gygi, "Conformational dynamics of the dimethyl phosphate anion in solution," *Chemical Physics Letters*, vol. 342, no. 3-4, pp. 434–440, 2001.

[66] D. J. Tobias, P. Jungwirth, and M. Parrinello, "Surface solvation of halogen anions in water clusters: An ab initio molecular dynamics study of the Cl-(H2O)(6) complex," *Journal of Chemical Physics*, vol. 114, no. 16, pp. 7036–7044, 2001.

[67] S. Raugei and M. L. Klein, "An ab initio study of water molecules in the bromide ion solvation shell," *Journal of Chemical Physics*, vol. 116, no. 1, pp. 196–202, 2002.

[68] I. Bako, J. Hutter, and G. Palinkas, "Car-parrinello molecular dynamics simulation of the hydrated calcium ion," *Journal of Chemical Physics*, vol. 117, no. 21, pp. 9838–9843, 2002.

[69] F. L. Gervasio, P. Carloni, and M. Parrinello, "Electronic structure of wet DNA," *Physical Review Letters*, vol. 89, no. 10, p. 108102, 2002.

[70] S. Piana, D. Sebastiani, P. Carloni, and M. Parrinello, "Ab initio molecular dynamics-based assignment of the protonation state of pepstatin A/HIV-1 protease cleavage site," *Journal of the American Chemical Society*, vol. 123, no. 36, pp. 8730–8737, 2001.

[71] F. Alber, G. Folkers, and P. Carloni, "Dimethyl phosphate: Stereoelectronic versus environmental effects," *Journal of Physical Chemistry B*, vol. 103, no. 29, pp. 6121–6126, 1999.

[72] T. J. Minehardt, N. Marzari, R. Cooke, E. Pate, P. A. Kollman, and R. Car, "A classical and ab-initio study of the interaction of the myosin triphosphate binding domain with ATP," *Biophysical Journal*, vol. 82, no. 2, pp. 660–675, 2002.

[73] A. Cavalli and P. Carloni, "Enzymatic GTP hydrolysis: Insights from an ab initio molecular dynamics study," *Journal of the American Chemical Society*, vol. 124, no. 14, pp. 3763–3768, 2002.

[74] K. Spiegel and P. Carloni, "Electrostatic role of phosphate 2485 in the large ribosomal unit from H-marismortui," *Journal of Physical Chemistry B*, vol. 107, no. 9, pp. 2091–2097, 2003.

[75] D. M. Benoit, D. Sebastiani, and M. Parrinello, "Accurate total energies without self-consistency," *Physical Review Letters*, vol. 87, no. 22, p. 226401, 2001.

[76] R. Resta, "Theory of the electric polarization in crystals," *Ferroelectrics*, vol. 136, no. 1-4, pp. 51–55, 1992.

[77] W. Zhong, R. D. King-Smith, and D. Vanderbilt, "Giant lo-to splitting in perovskite ferroelectrics," *Physical Review Letters*, vol. 72, no. 22, pp. 3618–3621, 1994.

[78] P. Ghosez, J. P. Michenaud, and X. Gonze, "Dynamical atomic charges: The case of ABO(3) compounds," *Physical Review B*, vol. 58, no. 10, pp. 6224–6240, 1998.

[79] P. Ghosez and X. Gonze, "Band-by-band decompositions of the Born effective charges," *Journal of Physics-Condensed Matter*, vol. 12, no. 43, pp. 9179–9188, 2000.

[80] M. Veithen, X. Gonze, and P. Ghosez, "Electron localization: Band-by-band decomposition and application to oxides," *Physical Review B*, vol. 66, no. 23, p. 235113, 2002.

[81] U. V. Waghmare, N. A. Spaldin, H. C. Kandpal, and R. Seshadri, "First-principles indicators of metallicity and cation off- centricity in the IV-VI rocksalt chalcogenides of divalent Ge, Sn, and Pb," *Physical Review B*, vol. 67, no. 12, p. 125111, 2003.

[82] D. Sebastiani and M. Parrinello, "A new ab-initio approach for NMR chemical shifts in periodic systems," *Journal of Physical Chemistry A*, vol. 105, no. 10, pp. 1951–1958, 2001.

[83] I. Souza, J. Íñiguez, and D. Vanderbilt, "First-principles approach to insulators in finite electric fields," *Physical Review Letters*, vol. 89, no. 11, p. 117602, 2002.

[84] P. Umari and A. Pasquarello, "Ab initio molecular dynamics in a finite homogeneous electric field," *Physical Review Letters*, vol. 89, no. 15, p. 157602, 2002.

[85] A. J. Williamson, J. C. Grossman, R. Q. Hood, A. Puzder, and G. Galli, "Quantum Monte Carlo calculations of nanostructure optical gaps: Application to silicon quantum dots," *Physical Review Letters*, vol. 89, no. 19, p. 196803, 2002.

[86] A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, "Surface control of optical properties in silicon nanoclusters," *Journal of Chemical Physics*, vol. 117, no. 14, pp. 6721–6729, 2002.

[87] K. M. Rabe and U. V. Waghmare, "Localized basis for effective lattice hamiltonians: Lattice Wannier functions," *Physical Review B*, vol. 52, no. 18, pp. 13236–13246, 1995.

[88] J. Íñiguez, A. Garcia, and J. M. Pérez-Mato, "Optimized local modes for lattice-dynamical applications," *Physical Review B*, vol. 61, no. 5, pp. 3127–3130, 2000.

[89] R. Caracas, K. M. Rabe, and X. Gonze, "Automatic generation of lattice Wannier functions," *in preparation*, 2003.

[90] I. Talanina and C. M. de Sterke, "Bloch waves and Wannier functions in periodic superstructure Bragg gratings," *Physical Review A*, vol. 62, no. 4, p. 043802, 2000.

[91] E. A. Ostrovskaya and Y. S. Kivshar, "Matter-wave gap solitons in atomic band-gap structures," *Physical Review Letters*, vol. 90, no. 16, p. 160407, 2003.

[92] M. Iannuzzi and M. Parrinello, "Wave-function localization in reciprocal space," *Physical Review B*, vol. 66, no. 15, p. 155209, 2002.

[93] R. Resta, "Quantum-mechanical position operator in extended systems," *Physical Review Letters*, vol. 80, no. 9, pp. 1800–1803, 1998.

[94] R. Resta and S. Sorella, "Electron localization in the insulating state," *Physical Review Letters*, vol. 82, no. 2, pp. 370–373, 1999.

[95] J. Zak, "Comment on "quantum-mechanical position operator in extended systems"," *Physical Review Letters*, vol. 85, no. 5, pp. 1138–1138, 2000.

[96] I. Souza, T. Wilkens, and R. M. Martin, "Polarization and localization in insulators: Generating function approach," *Physical Review B*, vol. 62, no. 3, pp. 1666–1683, 2000.

[97] E. Koch and S. Goedecker, "Locality properties and Wannier functions for interacting systems," *Solid State Communications*, vol. 119, no. 2, pp. 105–109, 2001.

[98] L. Bernasconi and P. A. Madden, "Optimally localized Wannier functions within the Vanderbilt ultrasoft pseudo-potential formalism," *Journal of Molecular Structure-Theochem*, vol. 544, pp. 49–60, 2001.

[99] Y. Wu, M. Manu, P. Giannozzi, N. Marzari, and R. Car, "Implementation of the maximally-localized Wannier functions in an ultrasoft Car-Parrinello molecular dynamics code," in *CP90 code*, Princeton University, 2001.

[100] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," *Physical Review B*, vol. 41, no. 11, pp. 7892–7895, 1990.

[101] K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, "Implementation of ultrasoft pseudopotentials in ab-initio molecular-dynamics," *Physical Review B*, vol. 43, no. 8, pp. 6796–6799, 1991.