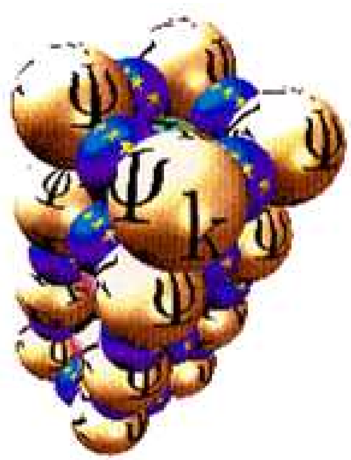
Ψ_k Newsletter

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

Number 94 August 2009



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Contents

1 Editorial

In this summer issue of the Psi-k Newsletter we have several reports on recent Psi-k supported workshops and one collaborative visit. These are followed by a number of job announcments and abstracts of newly submitted or recent papers.

The scientific highlight of this issue is by Leonardo Guidoni (L'Aquila), Carme Rovira (Barcelona) and Marialore Sulpizi (Cambridge) on "Ab initio methods for biological systems: state of the art and perspectives".

For further details on this newsletter, please check the table of content.

The *Uniform Resource Locator* (URL) for the Psi-k webpage is:

`http://www.psi-k.org.uk/`

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

The email address for contacting us and for submitting contributions to the Psi-k newsletters is

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2 Psi-k Programme

"Towards Atomistic Materials Design"

2.1 Reports on the Psi-k Supported Workshops

2.1.1 Report on the 4thInternational ABINIT Developer Workshop

Autrans (France)

24th– 27thMarch 2009

Psi-k Network, GdR-DFT and Scienomics

P. Blaise, D. Caliste*, T. Deutsch, L. Genovese and V. Olevano

`http://wwwold.abinit.org/2009-Abinit`

Initiated in 2002, the series of ABINIT developer workshops, organized each other year, plays an important role in the life of the ABINIT community. It is the occasion for the most active ABINIT developers, as well as a few expert users, and selected invitees, to gather and exchange information, and present recent developments. The future of ABINIT is also discussed, and recommendations are issued.

This year, the number of participants reached 56 people including four invited speakers from different other communities. This opening to developers outside ABINIT and their interesting contributions show the maturity of this software. These invited contributions were done in the field of post-ground state calculations with the talk about Yambo, a software for Many-Body calculations in solid state and molecular physics (A. Marini). The second talk in this field was about the capability to compute the Maximaly Localized Wannier Functions for accelerated band structure calculations with the help of the Wannier90 library (A. Mostofi). In these both cases, ABINIT is used as the fundamental tool to compute the ground state of the system. The second axis of the invited talks was about the improvement of ABINIT with the help of outside contributions. On one hand this was done with the presentation of a Linux distribution packager point of view about the package and its distribution (D. Berkholz) and on the other hand by the presentation of the XC library initially developped for Octopus software but on the way for inclusion inside ABINIT (M. Marques).

Beside these outside contributions, different labs implied in the development of ABINIT presented their contributions. One should remember two main axis. The first was about the ongoing effort to implement the missing functionnalities in the PAW formalism in comparison with the functionnalities of norm-conserving pseudo-potentials. This includes the non-colinear magnetism, the spin orbit coupling and the DFPT formalism (M. Torrent) ; but also the capability to simulate Mössbauer spectra and to compute the response to an electric or a magnetic field within the PAW formalism (J. Zwanziger) ; or also the development of the local exact exchange (F. Jollet). The second main axis was in the field of the GW approximation and its improvements (better paralllelism, method for fewer empty bands. . .) as presented by F. Bruneval and M. Giantomassi. Besides these two axis, several other points were discussed. One can cite the effort to port ABINIT to super-computers, with massively parallel network (F. Bottin), hybrid architectures (L. Genovese) or distributed computational power (M. Oliveira). Finally, several applications of the ABINIT program were presented, like the key exploration done by M. Mikami for warm-white led engineering, the *ab initio* explanation of the structure of GeMn nano-columns (E. Arras) or temperature dependance of the band energy in semiconductors (P. Boulanger).

The workshop was also the place for several discussions about the development of the ABINIT software. Among these talks, the documentation and user oriented tutorials and information were discussed around the availability and improvement of the new web site. One other discussion session was dedicated to the required decisions to continue the development of ABINIT with the same level of quality with an always growing software base and contributors. Indeed, ABINIT will need to enforce its coding standards and current code through a beautification phase to go to version 6 that will allow to continue to easily and safely add new functionnalities.

With all these diverse contributions, external, physics and software engineering, the meeting was considered by all the attendees as a very good working session resulting in several achievements. The full program is available on-line at

`http://wwwold.abinit.org/2009-Abinit`

as is also the list of the participants.

Programme

Tuesday 24th

12.30-14.00 **Lunch time**

14.00 **Introduction+SWOT**

Ch.: X. Gonze, T. Deutsch & G.-M. Rignanese

14.30 **PAW session:**

M. Torrent(25')
J. Zwanziger(25')

G. Jomard(A) (10')
A. Jacques (10' +10')

15:50-16.20 **Tea/coffee break**

16.20 **Correlated electrons:**

B. Amadon(25')
F. Jollet(25')
D. Adams (A) (10')

17.20 Build system

17.30 **Discussion (30')**

Mod.: J.-M. Beuken

Web

18.00-19.00 **Poster session**

Wednesday 25th

9.00 **Methodological developments:**

L. Genovese (25')
M. Mancini(25')
A. Lherbier(A) (10')
A. Romero (A) (10')

10.15-10.45 **Tea/coffee break**

10.45 **Links with communities:**

D. Caliste (25')
M. Marques (25')
A. Mostofi(25')

12.00 **Scienomics**

X. Krokidis (30')

12.30-14.00 **Lunch time**

14.00 **Software engineering:**

Ch.: M. Côté
X. Gonze (25')
J.-M. Beuken(25')

14.50 **Discussion (30')**

Mod.: M. Côté
An.: X. Gonze, J.-M. Beuken & A. Jacques
Merge/testing

15.20-15.50 **Tea/coffee break**

15.50 **Software engineering:**

Ch.: M. Côté

Y. Pouillon(25')
T. Deutsch(15')

16.30 **Discussion (30')**

Mod.: M. Côté
An.: T. Deutsch & Y. Pouillon
Build system

17.00 **Software engineering:**

Ch.: M. Côté

D. Berkholz (25')

17.25 **Discussion (25' +25')**

An.: A. Jacques, D. Berkholz & G.-M. Rignanese

Packaging
SWOT

18.25 **Advisory board**

19.00 **Poster session**

Thursday 26th

9.00 **Perturbation:**

Ch.: R. Caracas
P. Boulanger(25')
M. Torrent(25')
M. Verstaete (25')
F. Da Pieve (A) (10')

10.25-10.55 **Tea/coffee break**

J. Zwanziger(25')
P. Hermet(A) (10')

11.30 **Discussion (40')**

Mod.: R. Caracas
An.: X. Gonze, Y. Pouillon & M. Giantomassi
Beautification

12.10-14.00 **Lunch time**

14.00 **GW+BS:**

Ch.: M. Torrent

F. Bruneval(25')
M. Giantomassi(40')
T. Rangel (25')
M. Cazzaniga (A) (
10')

15.40-16.10 **Tea/coffee break**

16.10 A. Marini(25')

16.35 **High performance:**

F. Bottin(25')
M. Oliveira (25')
J. Laflamme (A) (10')

17.35 **Discussion (HPC) (55')**

Mod.: M. Torrent
An.: F. Bottin, L. Genovese, M. Oliveira & M. Côté

GPU
Multi-parallelism

Evening: **Social diner**

Friday 27th

9.00 **Applications:**

Ch.: J. Zwanziger

S. Blackburn(20')
P. Blaise (20')
E. Arras (20')

10.00 **Tea/coffee break**

R. Caracas (20')
M. Mikami(20')

11.10 **Discussion (80')**

Mod.: J. Zwanziger
An.: X. Gonze & Y. Pouillon

ABINIT6
Debriefing

12.30 **Lunch time**

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2.1.2 Report on the" KKR Workshop IV: Methodology and Applications"

June 12-14, 2009

Research Institute For Solid State Physics and Optics, Hungarian Academy of Sciences,
Budapest, Hungary

Sponsored by Psi-k, RISPO HAS, NEFIM

Organizers: B. Ujfalussy, L. Szunyogh, L. Udvardi, J. Kollar

Web page: `http://kkrws.phy.bme.hu`

The workshop was organized to continue the regular series of meetings of the Korringa-Kohn-Rostoker (KKR) research community organized under the support of Psi-K (Munich 2004, Bristol 2006, Canterbury 2008). The very purpose of the proposed workshop to keep the KKR method in the forefront of ab initio based computational materials science. by bringing together experts and students of leading groups in Europe, in the United States and in Japan to discuss recent advances related to the methodological developemnents in KKR, as well as current problems of condensed matter science.

Highlighted topics of the workshop were as follows:

(i) Methodological developements, with emphasis to large scale and full potential calculations. A special session focusing on these issues was devoted to the 60^{th} birthday of Rudi Zeller!

(ii) Functional materials for spintronics: oxides, half-metals and multiferroics.

(iii) Nanomagnetism and correlation effects in magnetic systems.

(iv) Finite temperature metallic magnetism in heterogeneous systems and nanostructured materials.

Program June 12, Friday

14:00 Welcome address (Laszlo Szunyogh, Balazs Ujfalussy)

Spintronics
14:05 Hisazumi Akai (Uni Osaka): New half−metallic antiferromagnets and their transport properties
14:30 Pawel Buczek (MPI Halle): Energies and life−times of magnons in half−metallic Heusler alloys
14:55 Dzidka Szotek (Daresbury): Structural phase transitions and fundamental band gaps $Mg_xZn_{1-x}O$ alloys from first principles

15:20 M. Carmen Muñoz (CSIC Madrid): Ferromagnetism at ZnO [0001] surfaces
15:45 Ingrid Mertig (MLU Halle): Ferroic Materials and Novel Functionalities

16:10−16:30 Coffee

Nanomagnetism, surface physics
16:30 Arthur Ernst (MPI Halle): Magnetism in nanostructures: first principles investigations with a multiple−scattering approach
16:55 Silvia Gallego (CSIC Madrid): Surface effects in the anisotropy of Co films
17:20 Juergen Henk (MPI Halle): Rashba−type spin splitting in surface alloys
17:45 Samir Lounis (FZ Juelich): Observation of subsurface defects with the electron focusing effect
18:10 Phivos Mavropoulos (FZ Juelich): Lifetime Reduction of Surface States Caused by Impurity Scattering

June 13, Saturday

Correlated systems
9:00 Martin Lüders (Daresbury): The different flavors of SIC in DFT
9:25 Walter Temmermann (Daresbury): Disordered Local Moment Description of Magnetism in 3d−monoxides and heavy 4f 's
9:50 S. Hossein Mirhosseini (MPI Halle): Self−interaction correction in Gadolinium: magnetic properties and surface states
10:15 Diemo Ködderitzsch (LMU Munich): Relativistic OEP for solids
10:40−11:00 Coffee

Spectroscopy
11:00 Jan Minar (LMU Munich): Correlation versus temperature: angle−resolved photoemission in the range between 10 eV and 10 keV
11:25 Ondrej Sipr (AS CR Prague): Role of valence−band correlations in XAS and XMCD spectra investigated via LDA+DMFT calculations
11:50 Masako Ogura (Uni Osaka): First−principles calculation of optical conductivity using the KKR−CPA method and Kubo−Greenwood formula

12:15 − 14:00 Lunch and Poster Session

Methodology, Full−Potential KKR
14:00 Rudi Zeller (FZ Juelich): Advances in the iterative solution of the TBKKR Dyson equation for large systems
14:25 Peter Weinberger (CNS Vienna): Describing surfaces: semi−infinite descriptions versus thin fim approaches
14:50 Hubert Ebert (LMU Munich): Solving the Poisson−equation within full−potential KKR calculations by means of Sacks's formula
15:15 Aurelian Rusanu & G. Malcolm Stocks (ORNL): Recent developments in Full−Potential MST at ORNL

15:40 Dmitry Fedorov (MLU Halle): Muffin−Tin Zero as a hidden parameter in the KKR method
16:05 Robert Hammerling (CMS Vienna): Magnetostatic energies in ab−initio magnetic anisotropy calculations

16:30 − 18:00 Coffee and Round−table Discussion

19:30 Banquet

June 14, Sunday

Magnetism
9:30 Balazs Gyorffy (Uni Bristol): KKR, Superconductivity and Magnetism
9:55 Sergeiy Mankovsky (LMU Munich): Exchange coupling tensor and its application to study magnetic properties of nanosystems using Monte Carlo simulation
10:20 David Bauer (FZ Juelich): Classical Spin Dynamics of Nanoclusters at Finite Temperature
10:45 Laszlo Udvardi (TU Budapest): Direct Monte−Carlo method for deposited magnetic nanostructures

11:10−11:30 Coffee

11:30 Laszlo Szunyogh (TU Budapest): Spin−Hamiltonian Based on the Relativistic Disordered Local Moment Scheme
11:55 Julie B. Staunton (Uni Warwick): The Relativistic Disordered Local Moment Theory of Magnetism: Magnetic Interactions in Heterostructures and Complex Lattices
12:20 Marcus Eisenbach (ORNL): Thermodynamics of magnetic systems from first principles: Combining Multiple Scattering ab initio methods (LSMS) with classical Monte−Carlo
12:45 Closing & lunch

Posters:
Stephan Lowitzer (LMU Munich): Calculating transport properties using the Kubo−Greenwood formalism
Corina Etz (MPI Halle): Ab−initio determination of the magneto−optical properties of $(\mathrm{Co}_m\mathrm{Ir}_m)$n on Ir(111)
Martin Gradhand (MLU Halle): Calculation of relativistic wavefunctions in the KKR method
Steven Walczak (MLU Halle): Non−equilibrium Green's function approach in the KKR formalism
Guntram Fischer (MLU Halle): Calculation of Magnetic Properties in Correlated Systems
Alberto Marmodoro (Uni Warwick): Electrons in systems with several types and degrees of disorder: the Non−Local Coherent Potential Approximation for multi−atom per unit cell materials
Ivetta Slipukhina (CEA Grenoble): Magnetic properties and Mn−Mn exchange interaction in some intermetallic Mn−Ge compounds
Eszter Simon (RISPO Budapest): Anisotropic Rashba splitting and consequences on impurity

interactions
Alexander Thiess (FZ Juelich): Massively Parallel Implementation of Lloyd's Formula
Manuel dos Santos Dias (Uni Warwick): Anisotropic Magnetic Correlations at Finite Temperature in RDLM

List of participants

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2.1.3 Report on Workshop on Nanoscale Carbon Materials

"Computational Studies of Defects in Nanoscale Carbon Materials"

CECAM-HQ-EPFL, Lausanne, Switzerland

May 11-13, 2009

CECAM, Psi-K, and Springer

Arkady Krasheninnikov, University of Helsinki and Helsinki University of Technology Savas Berber, Gebze Institute of Technology, Turkey David Tomanek, Michigan State University, USA

CECAM Home Page:

`http://www.cecam.org/workshop-0-313.html`

MSU Home Page: `http://nanotube.msu.edu/dnc09/`

Summary

The workshop "Computational Studies of Defects in Nanoscale Carbon Materials"(DNC09) took place in CECAM-HQ-EPFL, Lausanne, Switzerland, in May 2009. The workshop was followed by another workshop on a very close subject "Carbon and Inorganic Nanotubes", (CINN09). In fact one day was common, so that the presentations on the common day dealt with the scientific matters relevant to both workshops. The DNC09 workshop was attended by 39 participants (including the organizers) from all over the world. The financial support from CECAM (Euro 7,500), Psi-K (Euro 4,000) and Springer (Euro 500) made it possible to invite a considerable number of world-renown experts working on defects in nanoscale carbon materials. As the main idea behind this workshop was to bring together representatives of solid-state physics and materials science communities who use computational tools to discuss the state of our understanding of defects in carbon nanostructures, most speakers had theoretical background and concentrated on the theoretical progress. In addition to the theoretical advances, recent progress in the experiment was covered by several speakers. As detailed below, the latest and most important results in the field were presented by the speakers and by other participants during the poster session. In addition to the already published results, a considerable amount of new unpublished data was presented. The central point was the detrimental and beneficial roles of defects in the behavior of carbon nanosystems and related issues such as the production of defects under electron and ion irradiation, the characterization of defects by various techniques, and the engineering of the properties of carbon nanosystems by controllable introduction of defects through irradiation and by chemical methods. Such a combination of complementary topics (theory/experiment, theoretical method development/applications etc.) resulted in interesting and productive scientific discussion which should have a strong impact on the development of the field and could eventu-

ally give rise to new collaborations. Based on the enthusiastic feedback we have received from the participants of the workshop, we believe the event was a success. It should also be pointed out that the workshop attracted a considerable number of students and young postdocs, so that the event was also important in the context of young researcher training.

Scientific content of the workshop

As mentioned in the workshop proposal, defects in nanoscale carbon materials, such as nanotubes and graphene, may fully govern their mechanical and electronic properties. Moreover, defects may cause intriguing behavior including magnetism. Presence of defects in solids is in general believed to be mostly detrimental. This is also true for carbon nanomaterials: indeed, defects reduce the mechanical toughness and electronic conductance. However, there are beneficial effects of defects, including stiffening of loosely-connected nanotube networks or nucleation sites for structural transformations, which have been mostly overlooked. Be vice or virtue, defects in carbon nanomaterials require complete understanding at the microscopic level. The aim of the workshop was to bring together representatives of solid-state physics and materials science communities who use atomistic computer simulations to understand the role of defects in carbon nanostructures at the microscopic level, and discuss recent progress in our understanding of the role of defects. Besides this, several experts gave an overview of the state-of-the-art in the experiments.

The following main topics were addressed:

1. The types and abundance of point defects in nanostructured carbon materials, such as graphene, nanotubes, fullerenes, etc, identification of defects
2. Effect of defects on the electronic and mechanical properties of nano-structured carbon materials.
3. Production of defects in carbon nanotubes and graphene under irradiation.
4. Defect-mediated magnetism in nanostructured carbon materials.
5. Experimental studies of native and irradiation-induced defects in carbon nanosystems.

Although the main stress of the workshop was on simulations, the last topic was very important for establishing links between the simulation and experimental results and for finding out new simulations challenges.

Topic 1: The types and abundance of point defects in nanostructured carbon materials

This issue was addressed in the presentation by Florian Banhart, University of Strasbourg, France, who gave an overview of new experimental developments with a particular stress on graphene. He presented new results of experimental studies on point defects in carbon nanomaterials carried out in an aberration-corrected transmission electron microscope (TEM). Additional experimental information on the signatures of native and irradiation-induced defects in scanning tunneling microscopy (STM) images of carbon nanotubes was given by Oliver Groening, Swiss Federal Laboratories for Materials Testing and Research, Switzerland. They spoke about point defects such as vacancies and interstitials and their signatures in TEM and STM images. It was pointed out that due to high energetic barriers separating different atomic configurations in carbon nanomaterials the concentration of defects may be nonequilibrium under certain conditions.

From the viewpoint of theory, the discussion was continued by Steven Louie who spoke on density functional theory (DFT) simulations of defects in graphene nanoribbons and nanotubes and on how defects influence electronic transport in these materials. Oleg Yazyev, Swiss Federal Institute of Technology, Lausanne, Switzerland, gave further details of first-principles simulations of defects in nanocarbons, including defects in double-layer graphene and graphite. The overview of point defects was also given in the presentations of the workshop organizers, S. Berber, D. Tomanek and A. Krasheninnikov. Formally their presentations were in the CINN09 workshop, but as the talks were given on the "common" day, these presentations can be discussed in the context of the topics addressed at the DNC09 workshop. It was pointed out that sp2-bonded carbon nanomaterials have a unique ability to heal defects such as vacancy clusters by forming new bonds and mending the "holes" trough non-hexagonal rings.

Extended defects were discussed in the presentation by Irene Suarez-Martinez, Institut des Matériaux Jean Rouxel, France, and in part by Laszlo Forro, Ecole Polytechnique Fédérale de Lausanne, Switzerland. Carbon nanotube intramolecular junctions were addressed by Andres Ayuela, University of San-Sebastian, Spain. Such junctions, which normally give rise to interface states, are typically made of topological defects arising from the connection between tubes of different chiralities. As pointed out in the presentation, although interface states are commonly regarded as a drawback in device performance, they may actually provide a means of achieving diode behavior at the nanoscale.

Topic 2: Effect of defects on the electronic and mechanical properties of nanostructured carbon materials

This topic was addressed in the presentations by Susumu Saito, Tokyo Institute of Technology, Japan. He pointed out that doping of semiconducting nanotubes by boron and nitrogen atoms is an important process to make p-type and n-type semiconductor nanotubes. Experimentally, however, the atomically controlled substitutional doping into nanoscale materials including carbon nanotubes remains to be realized in the future. S. Saito also reported a study of the energetics and geometries of B and N-doped carbon nanotubes in the framework of the density functional theory. The electronic properties of impurity-induced states ("impurity levels") in B and N doped semiconducting carbon nanotubes were also studied in detail. Their spatial distribution is found to correlate well with the depth of the state from the top (bottom) of the valence (conduction) band. Deep states show rather narrow spatial distribution, while shallow states show wider distribution. This topic was also addressed in the presentations by S. Louie who pointed out that doping of naontubes with B and N atoms may give rise to the new localized states which do not directly contribute to the conductance. S. Louie and D. Tomanek also discussed the effects of defects at the edges of graphene ribbons on the spin-polarized transport in these systems. It was concluded that defects may be beneficial, as edge defects (in practice unavoidable, but different at different edges), may block spin-polarized current with a particular spin value, which may be useful for spintronics.

As for mechanical properties, Laszlo Forro presented experimental results on improvements of the bending modulus of carbon nanotube bundle due to electron irradiation. This happens through irradiation-induced covalent bonds between the nanotubes which prevent sliding, and give rise to an improvement of mechanical properties of nanotube samples: despite a small drop in the Young modulus and tensile strength due to vacancies, irradiation may have an overall positive effect. The theory of irradiation-mediated enhancement of mechanical properties of multi-walled nanotubes, nanotube bundles and nanotube bucky paper were presented by A. Krasheninnikov.

The electronic transport in pristine and defected nanotubes was discussed at length byJ.-C. Charlier, Université Catholique de Louvain, Belgium. He spoke on the modifications induced by various defects in the electronic properties of the carbon nanotubes, as reveled from first-principles calculations. As the defects also play a key role in the chemical reactivity of carbon nanotubes, the study of the modulation of the conductance due to specific molecules adsorbed at the defected nanotube surface was presented.

The effects of defects on the electronic properties of carbon nanomaterials were also discussed by Francesco Mercuri, University of Perugia, Italy, within the framework of a chemical approach. Finally, the influence of defects on the mechanical and electronic properties of carbon nanotubes was discussed by Gotthard Seifert, Dresden University of Technology, Germany, and a comparison to similar phenomena in non-carbon nanotubes was made, corroborated by a presentation focused on experimental studies of inorganic nanotubes by Dmitri Golberg, Japan.

Topic 3: Production of defects in carbon nanotubes and graphene under irradiation

Numerous experiments pointed out that controllable introduction of defects into the carbon network may give rise to new functional devices, e.g., carbon nanotube-based quantum dots. Irradiation is a suitable tool for creation of defects either in the whole sample or in certain parts using focused ion or electron beams. As for the latter, creation of defects by electron beam is particularly hot subject nowadays, as modern electron microscopes with aberration-corrected illumination systems allow the focusing of an electron beam onto a specimen area of 0.1 nm in diameter. Hence, it is not only possible to obtain images by scanning the beam over the specimen but also to irradiate the material in pre-determined areas with atomic-scale precision. As discussed by F. Banhart, atoms in graphitic structures can be displaced by electron beam with electron energies above 80 keV. Thus the transmission electron microscope can be used to create point defects or extended defect structures in graphitic nanomaterials in a controllable manner, so that this technique can be used for engineering the atomic and electronic structure of carbon system. The theoretical aspects of defect production under electron and ion irradiation as well as defect evolution were discussed by O. Yazyev, D. Tomanek, A. Krasheninnikov.

Topic 4: Defect-mediated magnetism in nanostructured carbon materials

Observations of magnetism in various metal-free carbon systems such as polymerized fullerenes and graphite have stimulated much experimental and theoretical research work on the magnetic properties of all-carbon systems. The driving force behind these studies was not only to create technologically-important, light, non-metallic magnets with a Curie point well above room temperature, but also to understand a fundamental problem: the origin of magnetism in a system which traditionally has been thought to show diamagnetic behavior only. The observed magnetism may originate from defects. Indeed, irradiation of graphite with protons resulted in a significant magnetic signal, which was explained in terms of vacancy-hydrogen interstitial atom complexes. The overview of this problem, along with DFT simulations of magnetic carbon systems with defects, was given by O. Yazyev.

A theoretical study of substitutional Ni, Co and Fe impurities in graphene was presented by Daniel Sanchez Portal, Centro de Fisica de Materiales, San Sebastian, Spain. It was shown that only Co atoms are magnetic with a magnetic moment of $\sim 1\mu$ B for the isolated impurity, and that the magnetic moment depends on the number of Co substitutions in A and B graphene sublattices. In contrast to Co impurities, Ni substitutional defects show a zero magnetic moment in flat graphene. However, Ni impurities develop a non-zero magnetic moment in metallic carbon nanotubes. This surprising behavior stems from the peculiar curvature dependence of the electronic structure of Ni impurities. It was concluded that magnetic/nonmagnetic transitions in systems with Ni impurities can be expected by applying anisotropic strain to a flat graphene layer.

Topic 5: Experimental studies of native and irradiation-induced defects in carbon nanosystems

The new developments in experiments were presented by F. Banhart, D. Golberg, O. Groening and non-invited participants of the workshop, as discussed above. The dialog between the theorists and experimentalist at the workshop was particularly important: the new unpublished experimental results posed new questions to the theorists, and the workshop was a very good opportunity to discuss new simulations challenges.

Unfortunately, due to three cancellations (Y. Miyamoto, M. Endo from Japan had to cancel their trips due restrictions introduced by their organizations in the light of swine flu; A. Rubio could not come due to personal matters), several important aspect of defects in nanostrucutred carbon materials (annihilation of defects during the growth of carbon nanotubes, spectroscopic characterization of defects) were not fully addressed. Nevertheless, based on presentations and discussion during the workshop, one can draw the following conclusions:

Main scientific conclusions:

- The level of theoretical understanding of defects in single-layer carbon nanomaterials such as graphene and single-walled carbon nanotubes is quite high, as evident from a good agreement between theoretical and experimental results. Less is known about defects in multi-walled carbon nanotubes or multi-layer graphene. The problem here is the rigorous account for van der Waals interaction between the graphitic sheets.
- sp2-bonded carbon nanomaterials have a unique ability to heal defects such as vacancy clusters by forming new bonds and mending the "holes" trough non-hexagonal rings.
- Due to high energetic barriers separating different atomic configurations in carbon nano-

materials the concentration of defects may be nonequilibrium under certain conditions.

- Defects in carbon nanomaterials can have an overall positive effect on the mechanical and electronic properties in carbon nanomaterials.
- Defect may give rise to magnetism in graphene and graphite, and the experimental results on the appearance of magnetic signal in carbon systems after irradiation can naturally be explained in terms of irradiation-induced defects.
- Controllable introduction of defects by electron and ion irradiation is a promising tool for tailoring the properties of nanostructured carbon materials.

Programme

Day 1 - May 11th, 2009
08:30 to 09:00 - Registration and Opening Remarks
09:00 to 09:45 A01-invited: Florian Banhart
The formation and observation of individual vacancies in carbon nanotubes by a focused electron beam
09:45 to 10:30 A02 - invited: Steven G Louie
Graphene nanostructures: Edges, ribbons, superlattices, and defective tubes
10:30 to 11:00 - Coffee Break
11:00 to 11:45 B - Summary Contributed Presentations
11:45 to 12:30 - Contributed Session B
12:30 to 14:00 - Lunch Break
14:00 to 14:45 C01- invited: Dmitri Golberg
Engineering of filled carbon nanotubes in a transmission electron microscope
14:45 to 15:30 C02 - invited: Susumu Saito
Energetics and Electronic Properties of Doped Carbon Nanotubes
15:30 to 16:00 - Coffee Break
16:00 to 16:30 D01- contributed: Irene Suarez-Martinez
Chemistry of different carbon nanoforms
16:30 to 17:00 D02 - contributed: Gueorgui Gueorguiev
Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide
17:00 to 17:30 D03 - contributed: Sami Malola
Edge reconstructions and gold in-plane of graphene

Day 2 - May 12th, 2009
09:00 to 09:45 E01- invited: Laszlo Forro
Extended defects in carbon nanotubes and graphene
09:45 to 10:30 E02 - invited: Chris Ewels
Metals on Carbon Nanotubes
10:30 to 11:00 - Coffee Break
11:00 to 11:45 F-Summary Contributed Presentations
11:45 to 12:30 - Contributed Session F

12:30 to 14:00 - Lunch Break
14:00 to 14:45 - G01 - invited: Oleg Yazyev
Defects in graphene and graphite: formation and magnetism
14:45 to 15:30 G02 - invited: Daniel Sanchez Portal
Substitutional Transition-Metal Impurities in Graphenic Nanostructures
15:30 to 16:00 - Coffee Break
16:00 to 16:45 - H01 - invited: Oliver Gröning
Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes
16:45 to 17:15 - H02 - contributed: Giulio Biddau
Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons
17:15 to 17:30 H03 - contributed: Andres Ayuela
Interface States in Carbon Nanotube Junctions: Rolling up graphene 18:30 to 23:00 - Conference Dinner

Day 3 - May 13th, 2009
09:00 to 09:45 J01 - invited: Jean-Christophe Charlier
Quantum Transport in Carbon Nanostructures including Defects
09:45 to 10:30 J02 - invited: Francesco Mercuri
Modeling of low-dimensional carbon nanostructures: an efficient approach based on chemical criteria
10:30 to 11:00 - Coffee Break
11:00 to 11:45 L01 - invited: Gotthard Seifert
The influence of Defects in Inorganic Nanotubes on Electronic and Mechanical Properties
11:45 to 12:30 - Closing remarks
12:45 to 14:00 - Lunch Break
14:00 to 18:00 - CINN09 Workshop

2.1.4 Report on Workshop on Transport in Nanostructures

"Theoretical Modeling of Transport in Nanostructures"

CECAM-HQ-EPFL, Lausanne, Switzerland

Jun 02, 2009 - Jun 05, 2009

CECAM, Psi-k and Quantum Wise

Magnus Paulsson and Víctor Manuel García-Suárez

`http://www.cecam.org/workshop-272.html`

The aim of the workshop "Theoretical Modeling of Transport in Nanostructures" was to bring together various groups related to the topic of ab-initio quantum transport that are currently developing and using different codes, mainly in Europe but also in the rest of the world. We focused on both the results and the codes themselves, in an effort to increase the applicability and efficiency of the codes and look for solutions to some of the problems faced by the community.

Current first-principles codes based on density functional theory (DFT) allow the calculation of the transport properties of systems with hundreds of atoms. These systems include molecules between metallic or semiconducting leads, atomic constrictions and chains, nanowires and nanotubes. The agreement between theory and experiments is getting better as the codes and theory improve and in most cases the differences between theory and experiment are within one order of magnitude. Several attempts have been made to increase the applicability of DFT methods, to include inelastic effects, spin degrees of freedom, non-collinear magnetism, the spin-orbit interaction, and beyond-DFT approaches like self-interaction effects, GW approaches, and time-dependent DFT (TDDFT). The aim at present is to develop feasible approaches to determine more accurately the transport properties of a wide range of molecules. Such approaches were reviewed and discussed extensively in the workshop.

The workshop was divided in four days and included 34 talks and more than 10 posters. The number of participants was 49 and included people from Europe, America, Asia and Australia. The most common topic in all talks and posters was ab-initio quantum transport based on a combination of Density Functional Theory and non-equilibrium Green's functions. There were also other topics related to quantum transport and the electronic structure of matter, which included condensed matter physics, strongly correlated systems and computational physics.

List of participants:

Carl-Olof Almbladh, Andrés Arnau, Marius Bürkle, Ioan Baldea, Harold Baranger, Peter Bokes, Giovanni Borghi, Supriyo Datta, Anna Delin, Mads Engelund, Ferdinand Evers, Mike Ford, Thomas Frederiksen, Michael Galperin, Amador Garíca Fuente, Aran García-Lekue, Victor Geskin, Björn Hardrat, Eva Marie Kalivoda, Olov Karlström, George Kirczenow, Andor Kormanyos, Tomasz Kostyrko, Colin Lambert, Alejandro López-Bezanilla, Jing-Tao Lu, Leonhard Mayrhofer, Eunan McEniry, Frederico Novaes, Pablo Ordejón, Juan José Palacios, Kyungwha Park, Fabian Pauly, Alessandro Pecchia, Alexandre Reily Rocha, Stephan Roche, Ivan Rungger, Daniel Sánchez Portal, Gabriele Sclauzero, Alexander Smogunov, Robert Stadler, Kurt Stokbro, Kristian Thygesen, Tchavdar Todorov, Alessandro Troisi, Yu Wang, Zeila Zanolli

Program

Day 1 - June, 2nd 2009

- 14:30 to 15:00 - Welcome
- 15:00 to 15:30 - Colin Lambert

  Controlled Electron Transport Through Single Molecules
- 15:30 to 16:00 - Harold Baranger

  Strong Correlations in Quantum Dots and Wires: Quantum Monte Carlo Studies
- 16:00 to 16:30 - Victor Geskin

  Partial vs. integer electron transfer in molecular assemblies: on the importance of multi-determinant theoretical description and the necessity to find a solution within DFT
- 16:30 to 17:00 - Coffee Break
- 17:00 to 17:30 - Mike Ford

  Density Functional based calculations for nanostructures containing large numbers of atoms
- 17:30 to 18:00 - Supriyo Datta

  Nanodevices and Maxwell's Demon

Day 2 - June, 3rd 2009

- 09:00 to 09:30 - Kurt Stokbro

  New developments for ab initio and semi-empirical modeling of quantum transport in electronic devices
- 09:30 to 10:00 - Michael Galperin

  Optical response of current-carrying molecular junctions
- 10:00 to 10:30 - Tomasz Kostyrko

  A quest for a molecular diode based on the mechanism of elastic scattering in asymmetric junctions
- 10:30 to 11:00 - Coffee Break

- 11:00 to 11:30 - George Kirczenow

  Theoretical Modeling of Transport in Molecular Nanostructures: A Pragmatic Approach

- 11:30 to 12:00 - Frederico Novaes

  Tunneling across a ferroelectric barrier: a first-principles study

- 12:00 to 12:30 - Fabian Pauly

  Controlling transport properties by molecular structure and light

- 12:30 to 15:00 - Lunch Break

- 15:00 to 15:30 - Ferdinand Evers

  Interplay of charging, conformation and magnetisation in metal (II) organic complexes: a DFT study

- 15:30 to 16:00 - Juan José Palacios

  Spintronics with graphene nanoribbons

- 16:00 to 16:30 - Ivan Rungger

  Bound and weakly coupled states in electron transport calculations

- 16:30 to 17:00 - Coffee Break

- 17:00 to 17:30 - Anna Delin

  Nanomagnetic phenomena in transition metal nanowires

- 17:30 to 18:00 - Tchavdar Todorov

  Can current drive an atomic-scale motor?

- 18:00 to 19:30 - Poster Session

Day 3 - June, 4th 2009

- 09:00 to 09:30 - Daniel Sánchez Portal

  Tilt angle dependence of electronic transport in molecular junctions of self-assembled alkanethiols

- 09:30 to 10:00 - Alessandro Pecchia

  NON-EQUILIBRIUM GREENS FUNCTIONS AND DENSITY FUNCTIONAL TIGHT-BINDING: A CRITICAL REVIEW AND PERSPECTIVES OF FUTURE DEVELOPMENT

- 10:00 to 10:30 - Kristian Thygesen

  Incorporating Exchange-Correlation Effects in Quantum Transport through Nano-scale Junctions

- 10:30 to 11:00 - Coffee Break

- 11:00 to 11:30 - Robert Stadler

  Interference effects and Fermi level alignment in electron transport through nitro-benzene nano-junctions

- 11:30 to 12:00 - Alessandro Troisi

  Microscopic Modelling of charge transport in molecular crystals, polymers and liquid crystals

- 12:00 to 12:30 - Thomas Frederiksen

  Electron-vibration couplings in single-molecule junctions

- 12:30 to 12:45 - Kurt Stokbro

  Software demonstration from QuantumWise A/S

- 12:45 to 15:00 - Lunch Break

- 15:00 to 15:30 - Peter Bokes

  Stroboscopic wavepacket basis for time-dependent quantum transport simulations

- 15:30 to 16:00 - Alexandre Reily Rocha

  Electronic transport in disordered systems: from gas sensors to spintronics

- 16:00 to 16:40 - Pablo Ordejón

  Transport in graphene layers connected by carbon nanotubes

- 16:30 to 17:00 - Coffee Break

- 17:00 to 17:30 - Kyungwha Park

  First-principles study of electron transport through the single-molecule magnet Mn12

- 17:30 to 18:00 - Carl-Olof Almbladh

  Kadanoff-Baym dynamics in strongly correlated nanostructures

- 20:00 to 23:00 - Dinner

Day 4 - June, 5th 2009

- 09:00 to 09:30 - Andrés Arnau

  Generalization of Bardeen's transfer Hamiltonian method to include inelastic currents due to electron vibration coupling

- 09:30 to 10:00 - Jing-Tao Lu

  Atomic dynamics in the presence of electronic current: Semi-classical Langevin equation approach

- 10:00 to 10:30 - Stephan Roche

  Computational Strategies to Tackle Mesoscopic Transport & Device Simulation in Complex Low-Dimensional Structures

- 10:30 to 11:00 - Coffee Break
- 11:00 to 11:30 - Alexander Smogunov

  Electron transport across locally magnetic nanocontacts
- 11:30 to 12:00 - Zeila Zanolli

  Defective carbon nanotubes: magnetism, spin transport and gas sensing applications
- 12:00 to 12:30 - Mads Engelund

  Heat Transport and Localized Vibrational Modes in Mono-Atomic Gold Chains
- 12:30 to 12:40 - Closing word

2.2 Reports on Psi-k Supported Collaborative Visits

2.2.1 Report on a Collaborative Visit of Manuel dos Santos Dias

Collaborative Visit of Manuel dos Santos Dias (University of Warwick) to the Department of Theoretical Physics of the Budapest University of Technology and Economics

I visited the group of Prof. László Szunyogh[1] in the Department of Physics of the Budapest University of Technology and Economics from May 11th to 22nd, 2009. The purpose of this visit was to establish a collaboration between his group and our group at the University of Warwick, headed by Prof. Julie Staunton [2]. We aim to develop and implement the formalism for the magnetic susceptibility obtained from linear response on the Relativistic Disordered Local Moment (RDLM) state. The visit was intended to last for a week, but fortunate circumstances allowed me to extended it for another week without additional costs.

Our proposed methodology is based on the Korringa-Kohn-Rostoker (KKR) method for electronic structure calculations, as developed in Multiple Scattering Theory language. This Green's function method is very suitable to treat systems in which one has to perform ensemble averages over configurations, either due to chemical disorder — using the Coherent Potential Approximation, or magnetic disorder — the Disordered Local Moment scheme. The non-relativistic description of the static magnetic susceptibility is well developed [3], while its relativistic counterpart was only partially treated, as of today [4,5]. The full relativistic extension of the theory will allow the exploration of effects related to the magnetic anisotropy of the systems under study, and this is the task that we intended to undertake, using a RDLM description. This is very relevant to my PhD work, as I focus on trying to understand which properties of exchange bias systems [6] can be derived from first-principles electronic structure calculations.

During my stay I was able to become proficient in the usage of the SKKR software package [7], which performs KKR calculations using the screened structure constants method on layered systems. Tests systems consisted of the Cu(100) surface, then with some Fe layers deposited on it. A bulk calculation for IrMn was also performed, by joining two semi-infinite systems of this material. Both ordered and DLM calculations were considered. After I was familiar with the SKKR package we could start implementing the new code, which will allow us to obtain anisotropic magnetic correlations in layered systems, at finite temperature. I had many fruitful discussions during my stay, on theoretical and practical aspects of the problem, and on alternative/complementary approaches to it.

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[1] http://www.phy.bme.hu/~szunyogh/

[2] http://www2.warwick.ac.uk/fac/sci/physics/theory/research/electrstr

[3] I.D. Hughes et al. Nature **446**, 650-653 (2007)

[4] J.B. Staunton *et al.*, Phys. Rev. Lett. **93**, 257204 (2004)

[5] J.B. Staunton *et al.*, Phys. Rev. B **74**, 144411 (2006)

[6] U. Nowak, in *Handbook of Magnetism and Advanced Magnetic Materials*, Vol.2, edited by H. Kronmüller and S. Parkin, Wiley, Chichester (2007), pp. 858–876

[7] L. Szunyogh *et al.*, Phys. Rev. B **49**, 2721-2729 (1994)

I am very grateful to the Psi-k network for making this visit possible. A special thank you goes to Prof. Alfréd Zawadowski, which made my extended visit possible, and to the warm hospitality I received from him and all the members of the Department of Theoretical Physics in Budapest.

3 General Job Announcements

Ph.D and Postdoctoral positions in Computational Materials Physics

University of Twente, Enschede, The Netherlands

4 PhD/**3 Postdoc** positions in Theoretical Condensed Matter Physics/Computational Materials Science are available for *graduates*/PhDs with a top grade in theoretical physics or chemistry to carry out research on

- First-principles Quantum Transport (Spin and Molecular Electronics)
- Novel Nano-Electronic Materials (Graphene; Oxide interfaces)
- Lightweight Hydrogen Storage Materials

The research is funded by the Dutch FOM (Fundamental Physics of Matter; 4 positions) and ACTS (Advanced Chemical Technologies for Sustainability; 1 position) research foundations and by the EU (2 positions). Common to all the projects is the use of ab-initio electronic structure calculations to study the physical properties (magnetic, optical and electrical) of condensed matter and to relate them to their chemical composition and atomic structure. Candidates will be expected

- to *acquire*/**have** a broad knowledge of theoretical condensed matter physics,
- to study in detail modern methods of electronic structure theory,
- to develop new theoretical methods in a form suitable for numerical implementation and
- to apply them in the relevant problem areas.

Experience with modern methods of electronic structure calculation is *desirable*/**necessary**. Successful candidates will get a contract for *4*/**1**+ years. The gross salary for a *PhD student* in the first year is *2,042.-* per month which will increase to *2,612.-* in the fourth year. For **postdocs**, salaries are in the range **2,861. - 3,755.-** per month depending upon experience.

Candidates *(PhD candidates should be no older than 26 years of age)* are invited to submit applications including a CV, list of university courses followed and grades obtained, **a list of publications** as well as the names and full contact details of 2 referees to:

Prof. P.J. Kelly,
Faculty of Science and Technology,
University of Twente,
P.O. Box 217,
7500 AE Enschede,
The Netherlands

E-mail: P.J.Kelly@utwente.nl
Tel.: +31-53-4893166
Homepage: http://cms.tnw.utwente.nl/

from whom particulars about each of the positions can be obtained.

Post-doctoral Research Position
in Molecular Dynamics and Nano-Metallurgy
ICB, Université de Bourgogne, Dijon, FRANCE

"Microscopic study of Nanometric Metallic Multilayer"

A Postdoc position is available for one year starting Mid September-October 2009.

Description:

A nanometric metallic multiplayer (N2M) A/B is constituted by alternated very thin slices of metals A-B-A- . This specific morphology induces a high reactivity which is used for technological purposes like welding of amorphous materials or sensitive components. N2M obtained by nano-deposition of metals are out of equilibrium systems. Their stability will depend on the competition between the excess of free, interfacial and elastic energies. Moreover the nanometric scale induces very strong composition gradients. It is especially interesting to study the reactive mechanisms associated with phase transformation at nanoscales under such non-equilibrium conditions when an exothermic front propagates in N2M. A microscopic approach is highly promising to understand these complex phenomena and molecular dynamics is especially suited for simulating the behavior of metals. During his(her) stay in our research team, the candidate will focus on the study by molecular dynamics of a N2M with a liquid/solid interface to understand how the microscopic properties influence the dynamical and structural formation of intermetallics.

Application:

The post-doctoral candidate should be familiar with computer sciences (classical molecular dynamics, computer programming) and/or physical metallurgy.

The position is open to non-French young PhD (less than 5 years) who have never received a salary in France for research activities.

The duration is one year. The net annual salary is 24,000 Euro.

The application deadline is 15th of July 2009.

The applications should include :

- Application letter highlighting relevant experience
- CV (mail, place and date of birth, nationality, marital status, personal address in the country of origin)
- List of publications

For further information and application submission, please contact:

florence.baras@u-bourgogne.fr
olivier.politano@u-bourgogne.fr

POST-DOC Position

IEMN-CNRS LILLE, France

We have an opening for a 1-year postdoc, to be carried out in the Theory Group at the IEMN (Institute of Electronics, Microelectronics and Nanotechnology) in Lille, France (http://theory.co.nr) starting October 2009. The project will be centered around the theory of contact mechanics and stretching of biomolecules (oligosaccharides, glycoproteins), and molecular adhesion on surfaces, studied by Molecular Dynamics and other atomic-scale simulation methods.

The successful applicant will have a PhD in physics, chemistry, materials science or related disciplines, with an adequate background knowledge of molecular physics, physical chemistry, condensed matter physics, statistical mechanics; experience in Fortran/C programming on Unix/Linux clusters; molecular visualization.

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fabrizio.cleri@univ-lille1.fr

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4 Abstracts

Magnetic ground state and multiferroicity in $BiMnO_3$

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Abstract

We argue that the centrosymmetric $C2/c$ symmetry in $BiMnO_3$ is spontaneously broken by antiferromagnetic (AFM) interactions existing in the system. The true symmetry is expected to be Cc, which is compatible with the noncollinear magnetic ground state, where the ferromagnetic order along one crystallographic axis coexists with the the hidden AFM order *and related to it ferroelectric polarization* along two other axes. The $C2/c$ symmetry can be restored by the magnetic field $B \sim 35$ Tesla, which switches off the ferroelectric polarization. Our analysis is based on the solution of the low-energy model constructed for the $3d$-bands of $BiMnO_3$, where all the parameters have been derived from the first-principles calculations. Test calculations for isostructural $BiCrO_3$ reveal an excellent agreement with experimental data.

Reference: JETP Letters **89** (2009) 701
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Electronic structure and ionicity of actinide oxides from first-principles calculations

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Abstract

The ground state electronic structures of the actinide oxides AO, A_2O_3 and AO_2 (A=U, Np, Pu, Am, Cm, Bk, Cf) are determined from first-principles calculations, using the self-interaction corrected local spin-density (SIC-LSD) approximation. Emphasis is put on the degree of f-electron localization, which for AO_2 and A_2O_3 is found to follow the stoichiometry, namely corresponding to A^{4+} ions in the dioxide and A^{3+} ions in the sesquioxides. In contrast, the A^{2+} ionic configuration is not favorable in the monoxides, which therefore become metallic. The energetics of the oxidation and reduction of the actinide dioxides is discussed, and it is found that the dioxide is the most stable oxide for the actinides from Np onwards. Our study reveals a strong link between preferred oxidation number and degree of localization which is confirmed by comparing to the ground state configurations of the corresponding lanthanide oxides. The ionic nature of the actinide oxides emerges from the fact that only those compounds will form where the calculated ground state valency agrees with the nominal valency expected from a simple charge counting.

(Submitted to Phys. Rev. B)

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Strain effects in group-III nitrides: deformation potentials for AlN, GaN, and InN

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Abstract

A systematic density functional theory (DFT) study of strain effects on the electronic band structure of the group-III nitrides (AlN, GaN and InN) is presented. To overcome the deficiencies of the local-density and generalized gradient approximations (LDA and GGA) the Heyd-Scuseria-Ernzerhof hybrid functional (HSE) is used. Cross-checks for GaN demonstrate good agreement between HSE and exact-exchange based G_0W_0 calculations. We observe a pronounced nonlinear dependence of band-energy differences on strain. For realistic strain conditions in the linear regime around the experimental equilibrium volume a consistent and complete set of deformation potentials is derived.

(submitted to: Appl. Phys. Lett.)
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Local investigation of femtosecond laser induced dynamics of water nanoclusters on Cu(111)

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Abstract

We explore the dynamics of low temperature interfacial water nanoclusters on Cu(111) by femtosecond-laser excitation, scanning tunneling microscopy and density functional theory. Laser illumination is used to induce single molecules to diffuse within water clusters and across the surface, breaking and reforming hydrogen bonds. A linear diffusion probability with laser fluence is observed up to 0.6 J/m^2 and we suggest that diffusion is initiated by hot electron attachment and detachment processes. The density functional calculations shed light on the detailed molecular mechanism for water diffusion that is determined by the local structure of the water clusters.

appeared in: Phys. Rev. Lett. **103**, 02610, (2009)

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Coupled cluster benchmarks of water monomers and dimers extracted from DFT liquid water: the importance of monomer deformations

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Abstract

To understand the performance of popular density-functional theory (DFT) exchange-correlation (xc) functionals in simulations of liquid water, water monomers and dimers were extracted from a PBE simulation of liquid water and examined with coupled cluster with single and double excitations plus a perturbative correction for connected triples [CCSD(T)]. CCSD(T) reveals that most of the dimers are unbound compared to two gas phase equilibrium water monomers, largely because monomers within the liquid have distorted geometries. Of the three xc functionals tested, PBE and BLYP systematically underestimate the cost of the monomer deformations and consequently predict too large dissociation energies between monomers within the dimers. This is in marked contrast to how these functionals perform for an equilibrium water dimer and other small water clusters in the gas phase, which only have moderately deformed monomers. PBE0 reproduces the CCSD(T) monomer deformation energies very well and consequently the dimer dissociation energies much more accurately than PBE and BLYP. Although this study is limited to water monomers and dimers, the results reported here may provide an explanation for the overstructured radial distribution functions routinely observed in BLYP and PBE simulations of liquid water and are of relevance to water in other phases and to other associated molecular liquids.

(submitted to: Journal of Chemical Physics)
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Theory of shape evolution of InAs quantum dots on $In_{0.5}Ga_{0.5}As/InP(001)$ substrate

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Abstract

In this work, the quantum dot (QD) formation of InAs on $In_{0.5}Ga_{0.5}As$/ InP(001) has been studied theoretically using a hybrid approach. The surface energies were calculated using density functional theory. For the elastic relaxation energies continuum elasticity theory was applied. This hybrid method, as already shown in the literature, takes into account the atomic structure of the various facets of the QDs as well as the wetting layer. Our study deals with the aspect of shape evolution of InAs QDs on a ternary substrate : It shows how the island shape close to equilibrium evolves with varying volume in $InAs/In_{0.5}Ga_{0.5}As/InP(001)$ epitaxy. Overall, our study indicates that for this system, there may exist two paths for island growth: one path involves an early energetic stabilization of flat, hut-shaped islands with high-index facets (that may persist due to kinetic limitations), while the other path invol ves islands with larger height-to-base ratio that develop low-index facets. At large volumes, the steeper, but more compact islands tend to be energetically mo re favorable compared to the elongated shapes.

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Structural stability and magnetic and electronic properties of $Co_2MnSi(001)/MgO$ heterostructures: A density functional theory study

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Abstract

A computational study of the epitaxial $Co_2MnSi(001)/MgO(001)$ interface relevant to tunneling magnetoresistive (TMR) devices is presented. Employing *ab initio* atomistic thermodynamics, we show that the Co- or MnSi-planes of bulk-terminated Co_2MnSi form stable interfaces, while pure Si or pure Mn termination requires non-equilibrium conditions. Except for the pure Mn interface, the half-metallic property of bulk Co_2MnSi is disrupted by interface bands. Even so, at homogeneous Mn or Co interfaces these bands contribute little to the minority-spin conductance through an MgO barrier, and hence such terminations could perform strongly in TMR devices.

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Two-dimensional electron gases: Theory of ultrafast dynamics of electron-phonon interactions in graphene, surfaces, and quantum wells

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Abstract

Many-particle electron-phonon interaction effects in two-dimensional electron gases are investigated within a Born–Markov approach. We calculate the electron-phonon interaction on a microscopic level to describe relaxation processes of quantum confined electrons on ultrafast time scales. Typical examples, where two-dimensional electron gases play a role, are surfaces and two-dimensional nanostructures such as graphene and quantum wells. In graphene, we find nonequilibrium phonon generation and ultrafast cooling processes after optical excitation. Electron relaxation dynamics at the silicon(001)2×1 surface exhibits two time scales, corresponding to intrasurface and inside bulk-scattering processes. For GaAs quantum wells, we present broad emission spectra in the terahertz range assisted by LO-phonons of the barrier material.

appeared in: J. Appl. Phys. **105**, 122409 (2009)
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Hubbard-U Band-Structure Methods

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Abstract

The last decade has seen a large increase in the number of electronic-structure calculations that involve adding a Hubbard term to the local density approximation band-structure Hamiltonian. The Hubbard term is then solved either at the mean-field level or with sophisticated many-body techniques such as dynamical mean field theory. We review the physics underlying these approaches and discuss their strengths and weaknesses in terms of the larger issues of electronic structure that they involve. In particular, we argue that the common assumptions made to justify such calculations are inconsistent with what the calculations actually do. Although many of these calculations are often treated as essentially first-principles calculations, in fact, we argue that they should be viewed from an entirely different point of view, viz., as phenomenological many-body corrections to band-structure theory. Alternatively, they may also be considered to be just a more complex Hubbard model than the simple one- or few-band models traditionally used in many-body theories of solids.

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Manuscript available from: cond-mat: arXiv:0907.1028 or email: svane@phys.au.dk

Absorption Characteristics of a Quantum Dot Array Induced Intermediate Band: Implications for Solar Cell Design

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Abstract

We present a theoretical study of the electronic and absorption properties of the intermediate band (IB) formed by a three dimensional structure of InAs/GaAs quantum dots (QD's) arranged in a periodic array. Analysis of the electronic and absorption structure suggest that the most promising design for an IB solar cell material, that will exhibit its own quasi-Fermi level, is to employ small QDs (∼ 6-12 nm QD lateral size). Use of larger QDs leads to extension of the absorption spectra into a longer wavelength region but does not provide a separate IB in the forbidden energy gap.

(Applied Physics Letters **93**, 263105 (2008)
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Excitonic and biexcitonic properties of single GaN quantum dots modelled by 8-band $\mathbf{k} \cdot \mathbf{p}$ theory

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Abstract

Excitons and biexcitons in GaN/AlN quantum dots (QD) were investigated with special emphasis on the use of these QDs for single photon source applications. The theoretical methodology for the calculation of single-particle states was based on 8-band strain-dependent envelope function Hamiltonian, with the effects of spin-orbit interaction, crystal-field splitting, piezoelectric and spontaneous polarization taken into account. Exciton and biexciton states were found using the configuration interaction method. Optimal QD heights for their use in single-photon emitters were determined for various diameter to height ratios. The competition between strong confinement in GaN QDs and internal electric field, generally reported in wurtzite GaN, was also discussed, as well as its effect on appearance of bound

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5 SCIENTIFIC HIGHLIGHT OF THE MONTH

Ab initio methods for biological systems: state of the art and perspectives

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Abstract

Ab initio quantum mechanical simulations of biological systems are expanding their capabilities to approach a variety of fundamental problems in biology. We review the progress on method development in the field achieved in the last years, focusing on emerging techniques that might become more relevant in the near future. A brief survey on recent applications in the field of enzyme catalysis and calculations of protein redox properties is also reported.

1 Introduction

In the last years biology entered the post-genomic era, expanding the research efforts from the single molecule studies to the extensive study of interplay between different biomolecules. A large effort is currently ongoing on protein networks and protein-protein interactions research with the main target to bridge the structural and biochemical properties of individual biological molecules with their collective behavior in cell cycles and signalling [1]. Bridging these scales is an fundamental step in the knowledge of biology and it will bring more quantitative description of biological phenomena, opening new perspectives in drug design, technology and medical research.

At the same time, and from the side of Biophysics and Structural Biology, a mechanistic approach to many biomolecules is made possible thanks to the growing availability of experimentally determined 3D molecular structures refined with atomic resolution. Using structural information, single molecule manipulation, and spectroscopy, is nowadays possible by experiments to unravel movements and electronic properties of living matter with accurate and time resolved details [2].

In this context, molecular modelling is also expanding its role. The understanding of the details at the atomic level of the interactions between proteins, nucleic acids, substrates, cofactors and drugs has acquired a renovated key role in the context of quantitative biology and post-genomics.

A variety of simulation techniques, ranging from electronic structure calculations to classical molecular dynamics (MD) and coarse grain models, has to be used to bridge the gap between spectroscopic data, structural information, and biological significance. The quantitative and detailed understanding of properties and molecular mechanisms of biomolecules has been recently the subject of different ab initio studies in the field of photoreceptors [3–6], electron transfer and redox proteins [7, 8], transition metal enzymes [9, 10], and computational (bio)spectroscopy (including optical, infrared, Raman, EPR, and NMR spectroscopy) [11–13].

From the point of view of the atomistic computer modelling, two levels of complexity will challenge our community for the next years: the intrinsic chemical complexity of the biomolecules and the necessity to cover the gap, in term of size and time, between what has to be simulated at the quantum level and all the rest of the (necessary) biological environment. The accuracy of ab initio molecular dynamics based on Density Functional Theory (DFT) is sufficient to provide a correct description of the electronic structure for large classes of biomolecules, but not always for specific sets of problems in the field of multi-center transition metal enzymes, photoreceptors and electron transfer proteins. The coupling between DFT-based ab initio MD and classical molecular dynamics, in the framework of Quantum Mechanics / Molecular dynamics simulations [14, 15], has successfully contributed to link the quantum properties of an active site to the whole biomolecular environment for a variety of systems [16–19].

Here we will shortly overview the computational methods used in the field of biomolecules mentioning also a selection of emerging methods that may have an increasing relevance in the future for the study of the electronic structure of biological systems. We also report a very limited number of applications, being conscious that it will not be able to cover important contributions to several active groups. Complementary and more complete surveys on ab initio modelling on biological systems can be found in a previous newsletter [20] and in several reviews on the subject [21–25].

2 Methods

2.1 Classical, Quantum and hybrid Quantum/Classical simulations

Dealing with electronic structure calculations of biomolecules cannot abstract from a description of the biomolecules at the level of classical molecular dynamics. The use of force-field based MD is indeed necessary, either to enhance the sampling of the conformational space or to include, using hybrid methods, the environment that cannot be described at the full quantum level because of computational costs. Classical, i.e. force-field based, setups of biological systems have typically $10^4 - 10^5$ atoms and a sampling of the phase space is crucial to overcome conformational and bond breaking/forming barriers. Enhanced sampling techniques can significantly improve the exploration of the phase space of biological macromolecules and reactive systems. Among the others, the recently developed metadynamics [26, 27] has been successfully used in biomolecular simulations coupled with classical [28, 29] and ab initio molecular dynamics [30, 31].

Ab initio molecular dynamics at finite temperature is commonly used to study biological systems in the framework of Density Functional Theory [32] because of the good compromise between chemical accuracy and computational costs. The choice of the exchange-correlation functional is crucial for many biomolecules. Gradient corrections are usually necessaries and different approaches may be preferred according to the kind of system and calculation performed. The popularity of BLYP functional [33, 34] comes from its capabilities to give a good description for hydrogen bonding systems [35, 36]. The B3LYP hybrid functional [37] can provide a better estimate of reaction barriers [38] but it has not been extensively used so far in ab initio MD because of the high computational cost of its implementation within a pure plane-wave scheme. Becke and Perdew [33, 39] functionals are preferred for transition metal complexes whereas Perdew, Burke and Ernzerhof functional [39] is more used in excited states calculations. Two alternatives are currently used in ab initio molecular dynamics: a pure plane wave (PW) approach and a Gaussian and plane wave (GPW) method [40–42]. In the PW method core electrons can be replaced using norm-conserving (Trouillier-Martins [43], Goedecker, Teter and Hutter [44]) and non-norm-conserving ultrasoft (Vanderbilt [45]) pseudopotentials. The Gaussian and plane wave method offers a convenient alternative, specially suited for the use of hybrid exchange-correlation functionals. Recent simulations of several tens of picoseconds on liquid water recently demonstrated the possibility to perform ab initio MD using B3LYP functional [46]. To circumvent the inability of current exchange-correlation functionals to incorporate dispersion forces, a pseudopotential scheme has been developed by the group of Rothlisberger [47, 48]. Higher angular momentum dependent terms of the pseudopotentials are optimized using correlated calculations references, obtaining very good results for weakly bound systems [49, 50] and liquid water [51].

Using hybrid Quantum Mechanics / Molecular Mechanics (QM/MM) approaches it is possible to limit the size of the part of the system that is described at the quantum level to the atoms belonging to the reactive part of the system (for instance the active site of the enzyme or the chromophore of a photoreceptor), whereas the rest of the atoms (protein and solvent) are treated at the classical force-field level. Quantum Mechanics and Molecular Mechanics system can be coupled in a fully Hamiltonian way using the scheme from Rothlisberger and coworkers [14, 15]. A recent extension of QM/MM techniques in the PWG approach is reported by Laino et al. [52, 53]. A more extensive method overview of QM/MM applications to biomolecules has been also reported in several reviews [20–25, 54].

It is interesting to note in the literature an expansion of ab initio MD techniques to the study of systems that were previously considered well described by classical mechanics. One example is represented by potassium channel proteins, usually treated at the level of classical mechanics since no bond breaking or forming processes is occurring during ion permeation through the channel pore. On the contrary, ab initio calculations demonstrated that the interaction between the permeating cations and the protein carbonyl ligands cannot be straightforwardly described by standard nonpolarizable force-fields [16,55,56]. In addition, the permeation mechanism is coupled with a proton transfer between surrounding ionizable residues [57] that cannot be modelled classically.

2.2 Calculations of redox properties

Redox properties can be calculated according to a MD method based on Marcus theory [58] as originally proposed by Warshel [59]. This scheme has been developed and implemented for use in DFT based ab initio molecular dynamics simulations [8, 60–64]. For a large class of proteins the ET activity falls within the Marcus regime, and the oxidation free energy (ΔA) and the reorganization free energy (λ) for the half reaction can be computed from ensemble averages of the vertical ionization energy (ΔE), according to the following equations:

$$\Delta A = \frac{1}{2}(\langle \Delta E \rangle_{red} + \langle \Delta E \rangle_{ox}) \tag{1}$$

$$\lambda = \frac{1}{2}(\langle \Delta E \rangle_{red} - \langle \Delta E \rangle_{ox}) \tag{2}$$

Subscripted angular brackets denote averages over equilibrium trajectories of the system in reduced (*red*) and oxidized (*ox*) state. In the hybrid scheme used for the study of redox properties in rubredoxin and which we review as an example here ΔE is still computed using DFT but the atomic configurations are extracted from classical simulations. The aim of the method is to combine the long time scale accessibility of the classical model with the quantum-mechanical methods to calculate ionization energies. When the size of the system does not permit a full DFT calculation a QM/MM approach can be used to calculate the energy of single configuration [7, 65].

For calculations of redox reactions in proteins an important issue is to have reliable starting structure for the initial configurations of the oxidized and reduced forms. Indeed proteins can undergo some major rearrangement upon oxidation/reduction which can be quite difficult to model.

Another issue regards the quality of our DFT description for the metal centers. In particular GGA functionals have been widely employed for calculations on biological systems, but they are not accurate enough for the description of metal centers where electronic correlation plays an essential role. In the case of rubredoxin, which we will discuss in a following section, the functional accuracy has been tested comparing electron detachment energies of small clusters ($Fe(SCH_3)_4$) with previous calculations and experimental data.

2.3 Emerging techniques

For many chemical and biochemical systems, DFT turned out to be a good compromise between method reliability and computational cost. Albeit this success in static calculations and ab initio molecular dynamics, the current approximations to the exchange-correlation functional are source of well-recognized and serious failures [66]. Systems where these limitations are evident are for examples, free radicals and transition metals with semi-filled $d-$shell (such as Cr, Mo, Fe, Ni, Mn) [67]. The drawbacks also affect the time dependent version of Density Functional Theory (TD-DFT) [68], causing unsatisfying estimates in the calculation of electronic excitations of a variety of molecular systems, one among the simplest being liquid water [69, 70]. The use of correlated quantum chemistry techniques, such as perturbative methods (MP2,MP4), coupled cluster (CC), and configuration interaction (CI) are limited to rather small biomolecules because the required computational resources grow very rapidly with the system size (see for instance ref. [71]). The searching for highly-accurate and size-scalable quantum algorithms will be in the next years a crucial challenge for the community working on ab-initio methods for biomolecules. An incomplete survey on emerging techniques is reported hereafter.

DFT extended schemes were proposed to study transition metal complexes because of the difficulties encountered by current functionals to correctly estimate the electronic correlation effects, especially in multi-center transition metal complexes. In the so called broken symmetry approach the spin coupling constant J between antiferromagnetically coupled metal centers is estimated by carrying out independent calculations for several spin configurations. The energy of all different spin states can be subsequently estimated using a Heisenberg Hamiltonian with coupling J. This technique has been successfully used to study iron-sulfur catalytic centers [72] and it has been recently extended and applied in an ab-initio molecular dynamics context [73]. The dynamical magnetostructural properties of the $2Fe - 2S$ iron-sulfur cluster of ferredoxin were studied using QM/MM [74], revealing the time-dependent interplay between the magnetic properties of the di-iron center and the protein environment. Another extension of DFT methods relevant for transition-metal active site chemistry is the DFT+U method, where a generalized-gradient approximation is augmented by a Hubbard U term [75]. A self-consistent DFT+U approach has been recently shown to successfully reproduce the electronic properties of the iron dimer and the spin and energetics of gas-phase iron-based reactions [76, 77]. Although not easily generalized to all transition-metal systems, both the above cited methods have the advantage that they require a computational effort comparable with that of plain DFT.

Green's function based methods, such as GW approximation and Bethe-Salpeter equation are traditionally used to calculate electronic excitations in condensed matter systems [78]. In a combined approach with classical molecular dynamics, these methods have been recently successfully extended to calculations of absorption spectra of liquid water [70, 79]. The excited state properties of the indole molecule, the aromatic component of the tryptophan amino-acid, has been also studied in solution by calculating electronic excitations using many body perturbation theory on snapshots extracted from a QM/MM simulation based on DFT [80]. These encouraging results suggests that Green's function methods can be suitable and affordable techniques to study the electronic excitations of other biomolecules that cannot be properly approached using TDDFT.

Another emerging technique in the field of biomolecule is Quantum Monte Carlo. It has been successfully employed in the past to compute ground-state properties of systems where electron correlations play a crucial role (see for instance the review [81]). An extended formulation has expanded its capabilities to investigate electronically excited states [82]. The QMC method, traditionally largely applied in many body physics and in Bose condensates, has been also used to correctly tackle difficult cases in quantum chemistry such as: radicals [83], transition metals [84, 85], electronic excited states [82, 86], anion-π and π-π interactions in aromatic molecules [87], van der Waals forces [88], and hydrogen bonding interactions [89, 90]. For hydrogen bonding systems, the water dimer dispersion curve was investigated both at the Variational Monte Carlo and at the Diffusion Monte Carlo level [90]. The experimental binding energy and the MP2 energy curve as a function of the distance between the two water molecules for the dimer were fairly reproduced. The physical interpretation of the resonating valence bond variational wave function offered also the possibility to dissect the covalent and dispersion van der Waals contributions to the H-bonding energy, estimated to be about 1.5 and 1.1 kcal/mol, respectively. The energetics of larger water clusters were also investigated by QMC and compared with MP2 and DFT [91]. From the side of electronic excitations, QMC calculations have shown to provide the correct excited state energy surface in one of the most representative example of TDDFT failure, the protonated Schiff-base model [82], which is a small analogue of the retinal protonated Schiff base,

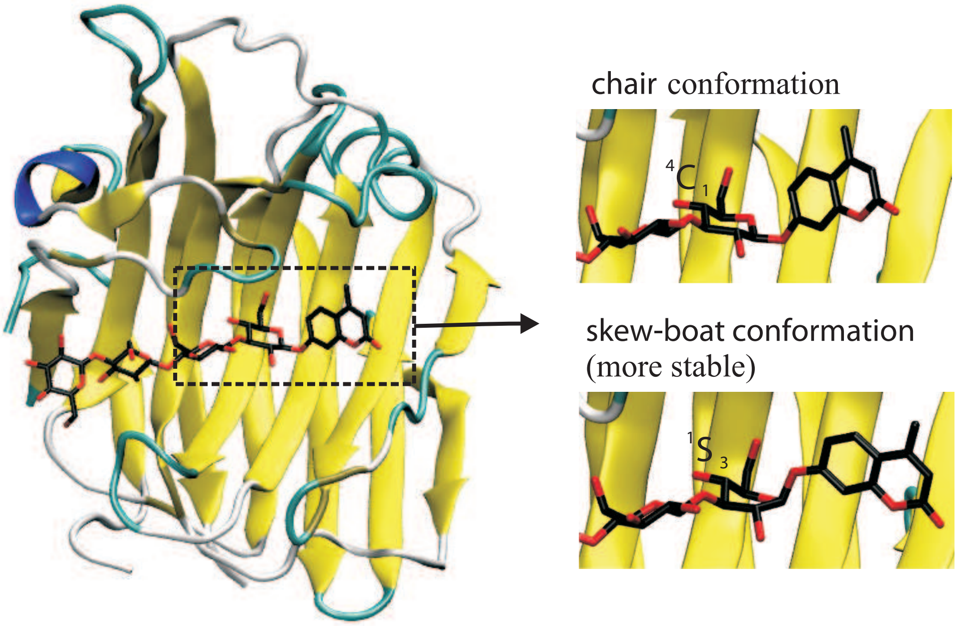

Figure 1: Minimum energy structures obtained from QM/MM simulations of the enzyme-substrate complex of Bacillus 1,3-1,4-β-glucanase, a family 16 glycoside hydrolase (Reference: Biarnes et al. J. Biol. Chem. 2006). The substrate (a 4-methylumbelliferyl tetrasaccharide) is shown in licorice representation.

the chromophore of rhodopsin.

3 Applications

3.1 Enzyme catalysis

The way enzymes perform its catalytic function has long fascinated not only biologists but also chemists and physicists [92–94], because subtle changes in the species involved (e.g. ligand, substrate, enzyme) may lead to serious diseases [95]. Therefore, elucidating how enzymes work at the atomic level is extremely relevant to find better drugs. Scientists have long sought the origin of the lowering of the activation energy barrier by enzymes, i.e. whether they stabilize the TS or raise the relative energy of the substrate (substrate preorganization [96]). Nevertheless, the molecular details of many enzymatic mechanisms still remain a mystery. Very often catalysis depends on the interplay between structure/electronic reorganization and dynamics. For instance, a distortion of one single sugar unit from a chair conformation to a boat-like is crucial for glycoside hydrolases to break the glycosidic bonds in carbohydrates. At the same time, the distortion raises the charge at the anomeric carbon and elongates the glycosidic bond distance, thus favoring catalysis [97] (Figure 1).

Another example is the binding of oxygen to myoglobin (Mb) and hemoglobin (Hb). The heme active center changes its electronic configuration upon binding, from a high spin (i.e. maximum number of unpaired electrons) to low-spin state, at the same time that the bond between the iron atom and the oxygen ligand develops [98]. The decomposition of the superoxide radical (O_2^-) into hydrogen peroxide and oxygen by superoxide dismutases, for instance, involves changes in the coordination state of the active species as well as in their oxidation states [95]. Deciphering these processes from an electronic point of view is necessary for understanding the mechanisms behind the enzymatic catalysis, as well as designing small molecules able to affect the biological function of the protein.

In the past few years, ab initio methods have contributed important insights into the catalytic mechanisms and structural features of a variety of enzymes (for recent reviews see e.g. [54]; [99]). This progress has been possible also because of the increased computer power, and the continuous development of techniques such as QM/MM and methods to accelerate sampling of free energy surfaces (metadynamics [26], transition path sampling [100] or steered molecular dynamics [101]). Because of the large number of ab initio applications to enzymes that appeared in the literature in the last few years, it is clearly impossible to review all of the work appeared so far. Here we will review only few representative examples, hoping to give a flavor of which problems can be addressed nowadays with ab initio methods. Metal-containing proteins represent almost half of the proteome of living organisms. Very often, the metal is present in the active site and plays a role in catalysis. Zinc metallo β-lactamases (MβLs) hydrolyze the β-lactam N-C bond of β-lactam antibiotics aided by one or two Zn^{2+} ions. Ab initio QM/MM simulations have shown that the flexibility of the Zn^{2+} coordination sphere plays a key role in the enzyme reaction [54, 102]. Mg^{2+} ions are present in several enzymes that hydrolyze chemical bonds such as epoxide hydrolase and ATPases [103]. In both cases, ab initio and QM/MM simulations including solvent water molecules in the QM region found that the water molecules assist the chemical reaction. These calculations were done in moderately large systems (about 50 QM atoms) but required large simulation times (100-200 ps). Similarly, two Mg^{2+} metals support the formation of a metastable intermediate along the reaction in ribonuclease H, but the role of solvent waters in mediating proton transfer events is crucial ([104]). All these works suggest the general importance of explicitly including solvation effects at the catalytic site for the correct description of an enzymatic mechanism at the atomic level.

Hemeproteins (metalloprotein containing a heme prosthetic group) are an important group of proteins and enzymes that carry out a variety of relevant biological functions, including oxygen transport and storage (hemoglobin and myoglobin), electron transfer (cytochromes), disproportionation of toxic hydrogen peroxide (catalases) and oxidation of substrates (peroxidases). This diversity of functions originates from the versatility of the heme group and the variety of interactions with protein scaffolds that generate different heme environments [105]. Because of the large size of the iron-porphyrin (38 atoms), ab initio calculations in hemeproteins are particularly demanding [106] (e.g. the iron-porphyrin, without the substituent groups forming the heme, plus several protein residues in its vicinity easily makes about 150 atoms) [107]. For the hybrid catalase-peroxidase, which contains a Met-Tyr-Trp adduct above the heme (essential for catalysis), the number of QM atoms to be included is about 250 [10]. During the last few years, a large effort has been devoted not only to characterize reaction intermediates with a complex electronic structure (e.g. the main reaction intermediate of the reaction cycle of peroxidases, catalases, cytochrome P450 and nitric oxide synthase is an oxyferryl-porphyrin cation radical named "compound I", Cpd I [107, 108]) but also in elucidating the mechanism of their formation/disappearance [108, 109]. For peroxidases, in which the active site is solvent-exposed, the mechanism of Cpd I formation was found to rely on the entrance of water molecules to the active site [109]. Again, this reinforces the active role that water molecules play in enzyme catalysis.

In contrast to peroxidases, the active site of catalases is buried in the protein. Catalase Cpd I reacts with hydrogen peroxide (H_2O_2) and decomposes it to H_2O and O_2 (Figure 2).

QM/MM metadynamics simulations have shown that there are two competing mechanisms to decompose hydrogen peroxide [9]. One of them is consistent with previous proposals based on structural information, whereas the other one explains the results of kinetic investigations on enzyme mutants.

Another problem in this field that has been investigated concerns the long-standing question of how myoglobin discriminates between poisonous CO and $\mathrm{O_2}$. During the past decade, it was demonstrated that CO distortion is not responsible for CO discrimination [110–112]. De Angelis et al. recently quantified the relevance of other factors, mainly hydrogen bonding of the bound oxygen [113]. A large effort has been also devoted to investigate how hemoglobins from different species bind oxygen [114]. Ab initio calculations have also contributed to understand the sometimes ambiguous iron-oxygen distances found in X-ray structures of heme proteins [107, 115, 116].

It should be taken into account that ab initio modeling of enzymes needs accurate structures as input. As the number of high resolution structures of complex systems increases, more accurate analysis can be performed. This is the case, for instance, of recent studies on membrane proteins [117–119], photoactive proteins [17, 120–122] or DNA-protein complexes. The recently solved X-ray structure of a complex between photolyase and a double-stranded DNA oligomer provided a suitable starting structure for performing computational studies to elucidate the mechanistic nature of the photochemical repair. QM/MM molecular dynamics simulations [123] elucidated the role of the various amino acids in the active site of the damaged DNA-enzyme complex.

3.2 Redox properties in proteins

Bio-inorganic oxidation/reduction enzymes and metalloproteins represent more than 40% of IUBMB classified proteins and are not only vital to biological energy conversion in photosynthesis and respiration, but are also critical to a growing number of signalling processes governing gene regulation and expression [124]. Understanding the mechanism of electron transfer (ET) between two metal sites or metal site and organic substrate is therefore of both theoretical and practical importance. The key question is how metalloproteins control which processes are thermodynamically feasible (i.e., reduction potentials) and how fast they occur (i.e., rate constants). Some of the issues that have been raised in this context concern the competition between short range effects, in essence the coordination chemistry of the metal ion, and long range effects, for example the reorganization of the protein, the placement of charged and polar residues, the access to the solvent. Related to this is the question of the relative importance of electronic relaxation effects, such as the difference between hard and soft ligands and electronic polarization of the

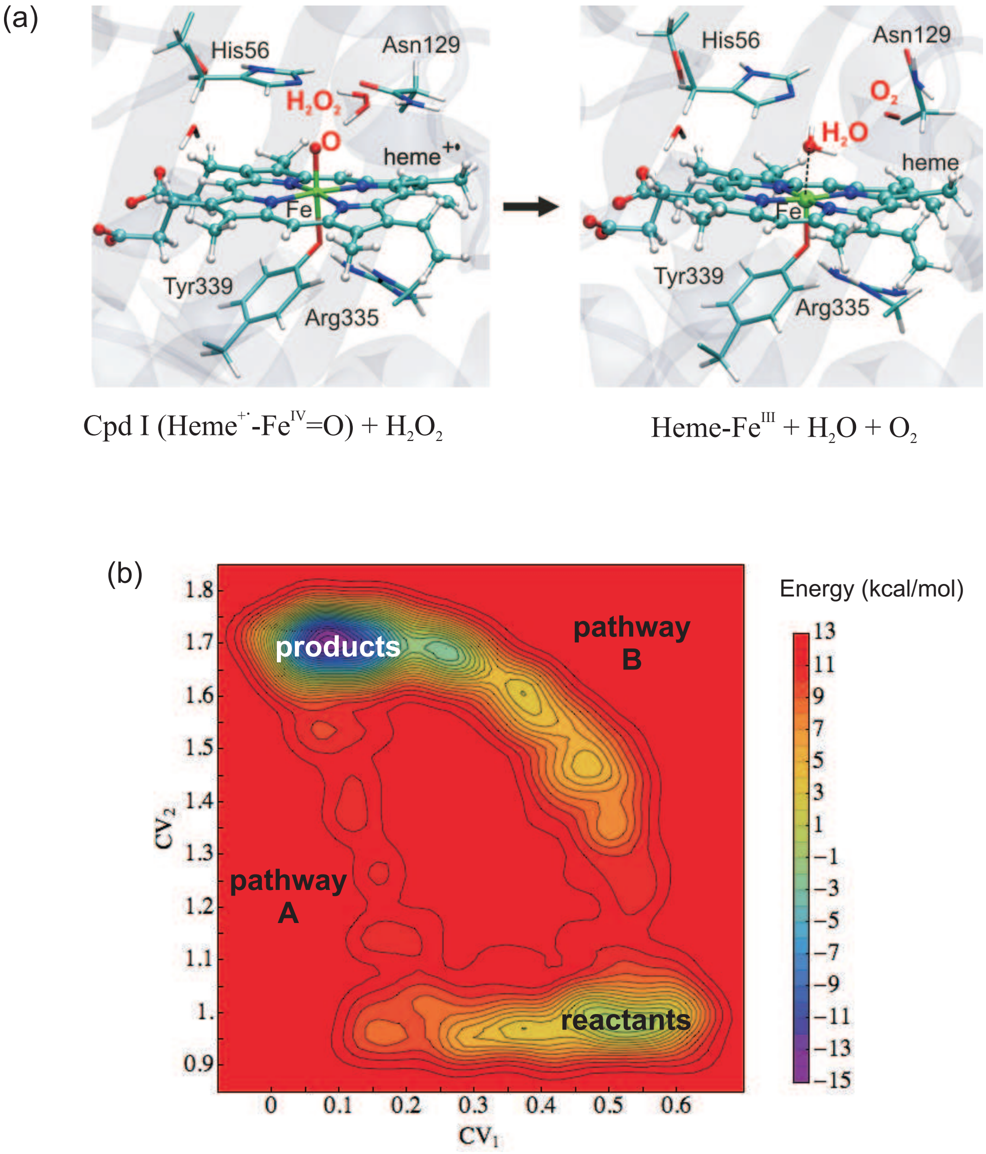

Figure 2: (a) The molecular mechanism of the catalase reaction (optimized structures of the reactants and products). (b) The corresponding reaction free energy surface obtained from QM/MM metadynamics simulations using two collective variables. Reference: Alfonso-Prieto et. al. J. Am. Chem. Soc. 2009.

protein, versus the reorganization due to atomic motion.

In this highlight we discuss as an example the calculations of redox properties of Rubredoxin(Rd) [8], a small and comparatively simple iron-sulfur protein. This is a particularly interesting case, since it is possible to combine a full ab initio description of the electronic structure of the protein in explicit solvent with sampling of the relevant time scale of the protein dynamics using a hybrid method based on a force field molecular dynamics / density functional theory scheme. Applying this scheme within the framework of Marcus theory [58] we are able to reproduce the experimental redox potential difference of 60 mV [125] between a mesophilic and thermophilic rubredoxin within an accuracy of 20 mV. The redox potential is modulated by the hydrogen bond interactions of the ligand cysteines with the NH groups of nearby residues with a stronger network of hydrogen bonds leading to more positive reduction potentials. We also compute the reorganization free energy for oxidation of the protein obtaining 720 meV for the mesophilic and 590 meV for thermophilic variant. Decomposition of the reorganization energy using the classical force field shows that this is largely determined by the solvent, with both short range (an oxidation induced change of coordination number) and long range (dielectric) contributions. The 130 meV higher value for the mesophilic form can be attributed to the different dielectric response of the solvent in the surrounding of the active site. These results underline the importance of a molecular description of the solvent and of a correct inclusion of polarization effects.

A major advantage of a DFT scheme here is that it accounts for electronic relaxation effects in response to oxidation/reduction. Such effects include ligand-metal charge transfer and the adjustment of hydrogen bond strength of coordinated protein residues and solvent. Within a DFT description of the vertical ionization energy for the entire solvated system, as applied here, also the instantaneous equilibration of electronic polarization to the new solute charge distribution is included. This can lead to a significantly lower estimate of the reorganization energy compared to a classical model with fixed charges.

We have shown that with modern computational methods calculations on a full small size protein are within reach and can offer a powerful predictive instrument to quantify properties, such as the reorganization energies, which are not easily measured by experiments.

4 Conclusions

In the last years electronic structure techniques and ab initio molecular dynamics have further expanded their capabilities to understand structure/function relationships of biomolecules to an increasing class of systems. In this brief review on the state-of-the art of methods and applications we have tried to make a survey on the last progresses in the field that might be representative but far from being complete. Two main problems are currently preventing ab initio calculations to tackle with success a wider class of challenging problems in biology: the size of the systems and the quality of the electronic structure methods. QM/MM methods are a first step to try to fill this gap and further development of multiscale methods is desirable in the future. We have also seen how different emerging quantum techniques seem promising starting points to go beyond standard DFT calculations. Thanks to this double effort, we may hope to tackle in the next years open questions in electron transfer, electronic excitations of photoreceptors, and

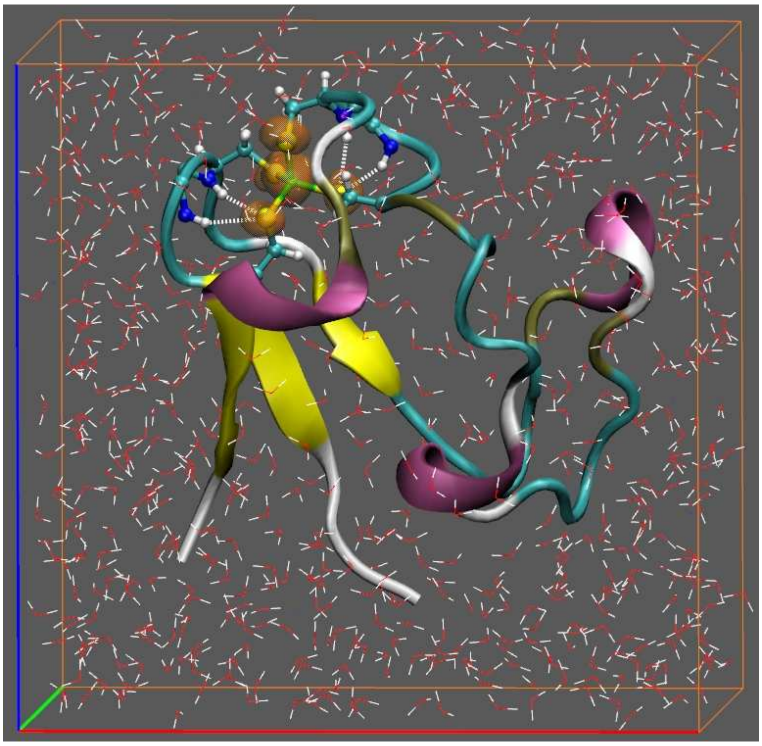

Figure 3: Representative MD configuration of rubredoxin generated from a 1IRO crystal structure [126] as employed in the DFT calculations. The periodically repeated simulation cell, with edges 31.136, 28.095, 30.502 Å contains the protein, 678 water molecules and 9 Na^+ counterions. The orange isosurface represents the spin density for the oxidized state (charge 0, spin 5/2) at 0.005 a.u.. Hydrogen bonds between sulfur atoms in the active center and nearby backbone NH groups are also highlighted.

multi-center transition metal proteins.

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