$\Psi_k$ Newsletter

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

Number 109 February 2012

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Sponsored by: UK's CCP's
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# Contents

# 1 Editorial

First of all a very Happy New Year to all!

Perhaps understandably, this first Psi-k newsletter of 2012 is dominated by reports on workshops supported by Psi-k and CECAM, which mostly took place in the later months of the last year. In addition we have also two workshop/school announcements, a report on a collaborative visit, a job announcement and a few abstracts of newly submitted or recently published papers.

The scientific highlight article of this issue is by Mark R Pederson (Washington DC) and John P Perdew (Tulane). Its title is "Self-Interaction Correction in Density Functional Theory: The Road Less Traveled". The highlight makes a very interesting reading and has been inspired by the last year's Psi-k/CECAM event on "Self-interaction correction: state of the art and new directions" which took place in Chester (UK) on 19-21 September 2011.

For further details please check the table of content of the newsletter.

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

| | **function** |
|---|---|
| **psik-coord@stfc.ac.uk** | **messages to the coordinators, editor & newsletter** |

Z (Dzidka) Szotek, Martin Lüders, Leon Petit and Walter Temmerman
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# 2 Psi-k Activities

### ”Towards Atomistic Materials Design”

## 2.1 Reports on the Workshops supported by Psi-k

### 2.1.1 Report on Strong Correlation from First Principles Workshop

**Kloster Seeon**

**30.8.-2.9.2011**

**ESF, Psi-k, DFG, CECAM**

**Patrick Rinke and Silke Biermann**

`http://www.fhi-berlin.mpg.de/th/Meetings/sc1p/index.php`

The workshop Strong Correlation from First Principles (SC1p) was held at Kloster Seeon from August 30 to September 2, 2011. The first-principles description of strongly correlated materials (typically materials containing partially filled d- or f-shells) is one of the great challenges in condensed matter physics. Strongly correlated materials such as complex oxides are becoming evermore important for technological applications, while simultaneously offering a plethora of physical phenomena (e.g. high temperature superconductivity) that continue to challenge our current understanding. Many disjointed approaches to tackle the problem are currently being pursued in the electronic structure community, by many-body theorists and quantum chemists. The SC1p workshop brought together 45 scientists from different communities who actively debated the very foundations of the challenges that lie ahead. The momentum generated by SC1p will be carried forward to a symposium with the same name at the March Meeting of the German Physical Society in Berlin in 2012 that has already been approved. The success of the SC1p workshop this year makes us confident that a series of workshops dedicated to the first principles treatment of strong correlations could develop. This series could provide the synergy to shape the future development in this important research area and would provide a unique opportunity to promote this emerging field in the European research landscape. 45 participants from leading international groups attended the workshop and presented 16 oral contributions (11 invited and 5 contributed talks) as well as 24 posters. Two overview talks on the first evening introduced the subject from two different angles. Over the course of the next three days invited experts presented their current results and insights into the topic. We had deliberately limited the time for presentations to 25min and reserved 20min for discussion after each presentation. For contributed talks the partition was 15min and 10min. This turned out to be an excellent idea, because it really encouraged lively discussion after each talk that continued into the coffee, lunch and dinner breaks. It also gave younger researchers the opportunity to participate in the discussions and to ask questions, which is often not the case at large conferences that permit only a limited number of questions that are then taken up by established scientists in the field.

Since two different communities with different philosophies and viewpoints came together in this workshop the discussions were very insightful for all participants. This was also the motivation for the round table discussion that took place Thursday morning. We had realized that many participants had submitted abstracts on the same materials system (transition metal monoxides). To spare the audience from having to hear the same introductory material several times, we decided to pool the presentations into one moderated round table, in which each speaker was given 5min to introduce the most important results or open problems. The ensuing discussion was active and productive (also thanks to the excellent moderation of G. Sawatzky) and makes us confident, that this format might be a viable alternative to the usual presentation style at scientific conferences.

Kloster Seeon in Bavaria provided the perfect venue for the workshop. The local organization at Kloster Seeon was smooth and extremely professional. The technical facilities in the conference room were state-of-the-art and easy to use. Posters were mounted in the coffee area and were on display for the whole duration of the workshop. This facilitated active discussions in front of the posters well beyond the time of the poster session on Wednesday evening. The fact that accommodation and conference facilities share the same premise at Kloster Seeon and that lunch and dinner were also served on site provided an informal atmosphere for stimulating discussions and gave conference attendants ample time to exchange ideas.

### Programme

**Tuesday, August 30**

| | |
|---|---|
| 19:00 - 20:15 | Dinner |
| 20:30 - 20:55 | Antoine Georges (CPHT-Ecole Polytechnique)<br>*Strong electronic correlations: what they are and how to treat them* |
| 20:55 - 21:15 | Discussion |
| 21:55 - 21:40 | Lucia Reining (LSI, Ecole Polytechnique)<br>*Correlation: coupling of excitations* |
| 21:40 - 22:00 | Discussion |

**Wednesday, August 31**

| | |
|---|---|
| 9:00 - 9:25 | Alexander Lichtenstein (University of Hamburg)<br>*Strong electronic correlations in real materials* |
| 9:25 - 9:45 | Discussion |
| 9:45 - 10:05 | Hong Jiang (Peking University)<br>*Electronic band structures of d- and f-electron systems from the GW@LDA+U perspective* |
| 10:05 - 10:20 | Discussion |
| 10:20 - 10:50 | Coffee Break |

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| 10:50 | - | 11:10 | Jan Kuneš (Institute of Physics, Praha)<br>*Multireference local states in solids with dynamical mean-field theory* |
| 11:10 | - | 11:25 | Discussion |
| 11:25 | - | 11:40 | Bernard Amadon (CEA - Département de Physique)<br>*An LDA+DMFT implementation in the projector augmented wave method: applications to f-electron systems* |
| 11:40 | - | 11:50 | Discussion |
|  |  |  |  |
| 12:00 | - | 14:00 | Lunch |
| 14:00 | - | 14:25 | Hardy Gross (MPI Halle)<br>*Density-matrix functional theory of strongly correlated solids* |
| 14:25 | - | 14:45 | Discussion |
| 14:45 | - | 15:10 | Xinguo Ren (Fritz-Haber-Institut, Berlin)<br>*Towards a general-purpose first principles method: a critical assessment of the random phase approximation and beyond* |
| 15:10 | - | 15:30 | Discussion |
|  |  |  |  |
| 15:30 | - | 16:00 | Coffee Break |
| 16:00 | - | 16:15 | David Jacob (MPI Halle)<br>*COHSEX+OCA and COHSEX+DMFT for nanoscopic conductors* |
| 16:15 | - | 16:25 | Discussion |
| 16:25 | - | 16:40 | Loig Vaugier (CPHT-Ecole Polytechnique)<br>*Hubbard U from the constrained random phase approximation (cRPA) within a full-potential linearized augmented plane wave approach: trends for 3d and 4d transition metal perovskites* |
| 16:40 | - | 16:50 | Discussion |
| 16:50 | - | 19:00 | Poster Session |
| 19:00 |  |  | Dinner |

**Thursday, September 1**

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|---|---|---|---|
| 9:00 | - | 9:20 | Sokrates Pantelides (Vanderbilt University)<br>*Density functional theory for d-electron systems - Are there really strong correlations?* |
| 9:20 | - | 9:35 | Discussion |
| 9:35 | - | 9:50 | Cyril Martins (CPHT-Ecole Polytechnique)<br>*Spin-orbital polarization in paramagnetic transition metal oxides:* $Sr_2IrO_4$ *versus* $Sr_2RhO_4$ |
| 9:50 | - | 10:00 | Discussion |
| 10:00 | - | 10:30 | Coffee Break |
| 10:30 | - | 12:00 | Round table discussion: transition metal monoxides<br>Chairman: G. Sawatzky |

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|---|---|
| | Contributors: Kuneš, Jiang, Gatti, Schroen, Thunstroem, Guzzo, Lichtenstein |
| | a) Short general introduction – 15 min – to MnO, NiO, FeO, CoO by chairman |
| | b) every speaker has max. 4 slides and max. 5 min |
| 12:00 | Lunch |
| | Excursion |
| 20:00 | Dinner |

### Friday, September 2

| | | | |
|---|---|---|---|
| 9:00 | - | 9:25 | George Sawatzky (UBC - Chemistry Department, Vancouver) |
| | | | *Effective coulomb and multiplet interactions in correlated electron systems: experimental determinations and importance of non uniform polarizability* |
| 9:25 | - | 9:45 | Discussion |
| 9:45 | - | 10:10 | Philipp Werner (ETH Zürich) |
| | | | *Dynamical screening in correlated electron materials* |
| 10:10 | - | 10:30 | Discussion |
| 10:30 | - | 11:00 | Coffee Break |
| 11:00 | - | 11:15 | Michele Casula (UPMC Paris) |
| | | | *Satellites and large doping- and temperature dependence of electronic properties in hole-doped* $BaFe_2As_2$ |
| 11:15 | - | 11:25 | Discussion |
| 11:25 | - | 11:50 | Giorgio Sangiovoanni (Vienna University of Technology) |
| | | | *Dynamical vertex approximation for nanoscopic systems* |
| 11:50 | - | 12:10 | Discussion |
| 12:15 | | | Lunch |

### List of participants

| | | |
|---|---|---|
| 1. | Amadon, Bernard, Dr. | Département de Physique Theorique et Appliquée, Arpajon, France |
| 2. | Ayral, Thomas | ETH Zurich, Zürich, Switzerland |
| 3. | Al Azar, Said M. S. | Computational Physics Lab, University of Jordan, Amman, Jordan |
| 4. | Bieder, Jordan | CEA – Département de Physique Theorique et Appliquée, Arpajon, France |
| 5. | Biermann, Silke, Prof. | CPHT-Ecole Polytechnique – Centre de Physique Theorique, Palaiseau, France |
| 6. | Caruso, Fabio | Fritz-Haber-Institute, Berlin, Germany |

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|---|---|---|
| 7. | Casadei, Marco | Fritz-Haber-Institute, Berlin, Germany |
| 8. | Casula, Michele, Dr. | UPMC - Institut de Minéralogie et de Physique des Milieux condensés, Paris, France |
| 9. | Chibani, Wael | Fritz-Haber-Institute, Berlin, Germany |
| 10. | Costi, Theo, Dr. | Research Centre Jülich - Institute for Advance Simulation, Jülich, Germany |
| 11. | Di Marco, Igor, Dr. | Uppsala University Physics Materials Theory Division, Uppsala, Sweden |
| 12. | Ederer, Claude, Dr. | Trinity College Dublin - School of Physics, Dublin, Ireland |
| 13. | Ekuma, Chinedu | Louisiana State University - Dept. Physics & Astronomy, Baton Rouge, USA |
| 14. | Fiorentini, Vincenzo, Prof. | Universit di Cagliari - Dipartimento di Fisica, Monserrato, Italy |
| 15. | Gatti, Matteo, Dr. | Universidad del Pais Vasco and ETSF - Nano-bio Group, Donostia, Spain |
| 16. | Georges, Antoine, Prof. | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 17. | Gross, Hardy, Prof. | MPI Halle - Microstructure Physics, Halle, Germany |
| 18. | Guzzo, Matteo | LSI, Ecole Polytechnique - Laboratoire des Solides Irradiés, Palaiseau, France |
| 19. | Hafermann, Hartmut, Dr. | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 20. | Hansmann, Philipp, Dr. | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 21. | Iori, Federico, Dr. | Universidad del Pais Vasco Dpto. de Qumicas. San Sebastián, Spain |
| 22. | Jacob, David, Dr. | MPI Halle Theory Department, Halle, Germany |
| 23. | Jiang, Hong, Prof. | Peking University - College of Chemistry, Beijing, China |
| 24. | Krapek, Vlastimil, Dr. | Institute of Physics Dept. Magnetism and Superconductors, Praha, Czech Republic |
| 25. | Krivenko, Igor | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 26. | Kuneš, Jan, Dr. | Institute of Physics Dept. Magnetism and Superconductors, Praha, Czech Republic |
| 27. | Lichtenstein, Alexander, Prof. | University of Hamburg Department of Physics, Hamburg, Germany |
| 28. | Martins, Cyril, Dr. | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 29. | Pantelides, Sokrates, Prof. | Vanderbilt University - Physics and Astronomy, Nashville, TN, USA |
| 30. | Reining, Lucia, Prof. | LSI, Ecole Polytechnique - Laboratoire des Solides Irradis, Palaiseau, France |
| 31. | Ren, Xinguo, Dr. | Fritz-Haber-Institute, Berlin, Germany |

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|---|---|---|
| 32. | Rinke, Patrick, Dr. | Fritz-Haber-Institute, Berlin, Germany |
| 33. | Rödl, Claudia, Dr. | LSI Ecole Politechnique, Palaiseau, France |
| 34. | Sangiovanni, Giorgio, Dr. | Vienna University of Technology - Institut of Solid State Physics, Vienna, Austria |
| 35. | Sawatzky, George, Prof. | UBC - Department Chemistry, Vancouver, British Columbia, Canada |
| 36. | Scheffler, Matthias, Prof. | Fritz-Haber-Institute, Berlin, Germany |
| 37. | Schrön, Andreas | Friedrich-Schiller-Universität - Institut fr Festkörpertheorie optik, Jena, Germany |
| 38. | Strand, Hugo | University of Gothenburg - Department of Physics, Göteborg, Sweden |
| 39. | Taranto, Ciro | Vienna University of Technology - Institut of Solid State Physics, Vienna, Austria |
| 40. | Thunstroem, Patrik | Uppsala University Physics Materials Theory Division, Uppsala, Sweden |
| 41. | Uijttewaal, Matthje, Dr. | TU-Clausthal - Theoretical Physics Clausthal-Zellerfeld, Germany |
| 42. | van Roekeghem, Ambroise | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau |
| 43. | Vaugier, Loig | CPHT-Ecole Polytechnique - Centre de Physique Theorique, Palaiseau, France |
| 44. | Werner, Philipp, Dr. | ETH Zürich - Department for Material Theory, Zürich, Switzerland |
| 45. | Wilhelm, Aljoscha | University of Hamburg Department of Physics, Hamburg, Germany |

### 2.1.2 Report on Workshop “Challenges and solutions for GW calculations in complex systems”

**CECAM, Lausanne**

**7-10 June 2011**

**CECAM, Psi-k, ESF**

**F. Giustino, A. Rubio, P. Umari**

## Workshop Summary

The Workshop ”Challenges and solutions in GW calculations for complex systems” was meant to be an opportunity to (1) bring all the major players in the GW method up to date in the most recent developments in the field, (2) review the available software implementations, (3) define standardization criteria to render the comparison between GW calculations from different codes meaningful, and (4) identify future major challenges in the area of quasiparticle calculations.

We had two talks describing quasiparticle calculations of defect energies in semiconductors and oxides (Louie, Bruneval). We had four talks on the use of GW calculations for metal/molecule contacts and for quantum transport calculations: Hybertsen (reporting also on new static approximations to the self-energy), Neaton (interfacial energy-level alignment and effect of off-diagonal matrix elements of the self-energy), Ferretti (off-diagonal corrections to the GW self-energy in quantum transport), Thygesen (fully self-consistent GW calculations for metal/molecule interfaces on localized Wannier basis). Three talks focused on the use of self-consistent GW: Van Schilfegaarde (review of the formalism and application to magnetic systems), Rinke (all-electron self-consistent GW), Thygesen (GW calculations for quantum transport). Two talks focussed specifically on the use of GW techniques for correlated electron system (Miyake, Gatti), and three talks reported on total energy calculations based on the GW method (Godby, Rinke, Ismail-Beigi). We had five talks on GW calculations without empty states (Louie, Galli, Huebener, Umari, Berger). These talks stimulated an intense discussion as described in the following section. All-electron GW calculations were reported by Ambrosch-Draxl, who performed a very systematic comparison between all-electron and pseudopotential calculations. We also had reports on the use of Coulomb truncation techniques (Martin-Samos), the use of GW for spin-dependent transport (Bluegel), X-ray spectroscopy (Rehr), the accuracy limit of GW calculations set by zero-point vibrations of the lattice (Marini), an update on the recent controversy about the electronic structure of ZnO (Rignanese), self-consistent solutions of the Dyson and Kadanoff-Baym equations (Stan), and applications to graphitic systems (Lebegue).

There has been an ongoing discussion throughout the workshop about the need of removing unoccupied states from the calculations of the screened Coulomb interaction. Several speakers proposed interesting strategies: approximations of the Kohn-Sham states at high energy using symmetrized planewaves and diffuse orbitals (Louie), use of an effective energy technique (Berger), use of a small number of dielectric eigenvalues obtained by iterative diagonalization (Galli), the use of the self-consistent Sternheimer method (Huebener), and the use of the Lanczos recursion method (Umari). There is a consensus on the need of eliminating empty states in order to bring GW calculations on systems with hundreds of atoms. Another interesting discussion took place around the accuracy of localized basis sets for calculating the GW self-energy.

Several speakers reported on the use of localized basis sets (Rinke, Thygesen, Umari, Bluegel, Huebener), although no systematic tests on the convergence with basis sets were reported. An important point of the workshop has been to try and establish the accuracy of GW quasiparticle calculations. On the optimistic end we heard of accuracies around 0.2-0.3 eV (most speakers), but for instance in the case of ZnO the results appear rather sensitive to the convergence with empty states and to the method used for carrying out frequency integrations (Rignanese). Also it was pointed out that claiming an accuracy below 0.2-0.3 eV may not be meaningful if we consider that lattice vibrations may lead to zero-point effects which may go up to 0.6 eV (Marini, Giustino).

This workshop has been extremely successful insofar the main groups active in the area of GW calculations (both development and application) were represented, and also the discussions were lively and motivating. The workshop highlighted a recent trend across all groups to make a substantial effort in order to render their software and calculations reproducible. As anticipated in the workshop proposal, there is a growing need to standardize the technical details of GW calculations and the corresponding software implementations. It is likely that this workshop will lead to define quality control strategies in the near future, and in this sense maybe a follow-up workshop in 2013 focussing entirely on validation and standardization would be in order. We point out that our unusual workshop format, comprising of 25 min talks followed by 20 min discussions, proved very successful. Indeed all participants appreciated the opportunity for in-depth discussions following each talk, and the workshop resembled more of an intense round-table discussion than a showcase for the results of individual groups.

In addition, this workshop has been so successful that the Editors of the European Physical Journal B have offered us the opportunity to edit a Special Issue of their journal reporting on the key advances in the area of GW calculations as presented within this workshop.

## Workshop Programme

### Day 1 - Tuesday June 7, 2011

14:00 to 14:10 Welcome

Session I : Introduction

14:10 to 14:55 - Steven G. Louie: GW method for defects, nanostructures, and molecular systems: recent progress and challenges

14:55 to 15:40 - Mark Hybertsen: New static approximations in the GW approach

15:40 to 16:05 - Coffee Break

Session II: Total energy

16:05 to 16:50 - Takashi Miyake: Constrained RPA method for correlated electron systems

16:50 to 17:35 - Sohrab Ismail-Beigi: The GW-RPA correlation energy and Luttinger-Ward theory: exact rewriting, systematic approximations and fundamental challenges

17:35 to 18:20 - Patrick Rinke: All-electron GW ground and excited state calculations in a localized basis

**Day 2 Wednesday June 8, 2011**

Session III: Unoccupied states A

9:00 to 9:45 - Giulia Galli: GW and BSE calculations without explicit calculations of empty electronic orbitals

9:45 to 10:30 - Hannes Hbener: Progress on Sternheimer-GW using local orbitals basis sets

10:30 to 11:00 - Coffee Break

Session IV: Methodological advances A

11:00 to 11:45 - Rex Godby: Algorithmic and physics options for improving GW-type calculations

11:45 to 12:30 - Adrian Stan: Algorithms for self-consistent solutions of the Dyson and Kadanoff-Baym equations. Equilibrium and the time-dependent properties of inhomogeneous systems.

12:30 to 14:00 - Lunch

Session V: Methodological advances B

14:00 to 14:45 - Mark van Schilfgaarde: Reduced Hamiltonians from the quasiparticle self-consistent GW approximation and applications

14:45 to 15:30 - Matteo Gatti: Metal-insulator transitions in the GW approximation: beyond a quasi-particle description

15:30 to 16:15 - Fabien Bruneval: The GW approximation when the number of particles changes for real

16:15 to 16:45 - Coffee Break

Session VI: Poster presentations

16:45 to 19:00 - Poster presentation

**Day 3 Thursday June 9, 2011**

Session VII: All-electrons methods

9:00 to 9:45 - Stefan Blgel: The GW approximation in the FLAPW method: towards magnetic systems

9:45 to 10:30 - Claudia Ambrosch-Draxl: The impact of widely used approximations to the G0W0 method: an all-electron perspective

10:30 to 11:00 - Coffee Break

Session: VIII: Unoccupied states B

11:00 to 11:45 Paolo Umari: The GWL method: GW calculations without empty states

11:45 to 12:30 - Berger Arjan: The effective-energy technique: GW calculations without summing over empty states.

12:30 to 14:00 - Lunch

Session IX: Transport

14:00 to 14:45 - Jeff Neaton: Electronic energy-level alignment at metal-organic interfaces with GW approaches

14:45 to 15:30 - Andrea Ferretti: Hybrid functional and GW corrections to quantum transport calculations

15:30 to 16:15 - Kristian Thygesen: Fully self-consistent GW calculations for metal-molecule interfaces: level alignment and electron transport

16:15 to 16:45 - Coffee Break

Session X: Spectroscopy

16:45 to 17:30 - John Rehr: Many-pole models of inelastic losses and satellites in x-ray spectra

17:30 to 18:15 - Andrea Marini: Giant zero-point-motion effects in carbon-based nanostructures

20:00 Dinner

**Day 4 Friday June 10, 2011**

Session XI: Applications

9:00 to 9:45 - Gian-Marco Rignanese: What is the G0W0 band gap of ZnO ?

9:45 to 10:30 - Michael Rohlfing: Excited electronic states from a perturbative LDA+GdW approach

10:30 to 11:00 - Coffee Break

11:00 to 11:45 - Layla Martin-Samos: Wigner-Seitz cell cutoff to handle Coulomb divergences in anisotropic systems

11:45 to 12:30 - Sebastien Lebegue: Advanced computational methods for the study of functionalized graphene and graphite

12:30 to 12:45 - Closing word

## List of participants

### Organizers

Giustino Feliciano
University of Oxford, United Kingdom

Rubio Angel
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Umari Paolo
CNR-IOM Democritos, National Simulation Center, Trieste, Italy

## Participants

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Antonius Gabriel  Catholic University of Louvain, Belgium
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Azadi Sam - Johannes Gutenberg University, Mainz, Germany
Baroni Stefano - International School for Advanced Studies (SISSA), Trieste, Italy
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Bruneval Fabien  CEA-Saclay, France
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Chiodo Letizia - Italian Institute of Technology, Lecce, Italy
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Hussain Tanveer - Uppsala University, Sweden
Hybertsen Mark - Brookhaven National Laboratory, USA
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Ismail-beigi Sohrab - Yale University, New Heaven, USA
Lambert Henry - University of Oxford, United Kingdom
Lebegue Sebastien - University of Nancy, France
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Marini Andrea - University of Rome II ”Tor Vergata”, Italy
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Pavone Pasquale - University of Leoben, Austria
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Rignanese Gian-Marco  Catholic University of Louvain, Belgium
Rinke Patrick  Fritz-Haber of the Max-Planck Society, Berlin, Germany
Rohlfing Michael - University of Osnabrck, Germany
Sakuma Rei - Chiba University, Japan
Sommer Christoph - University Mnster, Germany

Stan Adrian - University of Jyvaskyla, Finland
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van Schilfgaarde Mark - Arizona State University, Tempe, USA
van Setten Michiel - Karlsruhe Institute of Technology, Germany
Waroquiers David - Catholic University, Louvain, Belgium
Windiks Ren - Materials Design, Inc., Montrouge, France
Yan Jun - Technical University of Denmark, Lyngby, Denmark
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### 2.1.3 Report on the "15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods"

**Trieste (Italy)**

**January 13-15th, 2011**

**The Abdus Salam International Centre for Theoretical Physics (ICTP)**
**CNR-IOM Democritos Simulation Center**
**Psi-k Network**
**International School for Advanced Studies (SISSA)**
**Centre Européen de Calcul Atomique et Moléculaire (CECAM)**
**Asia Pacific Center for Theoretical Physics (APCTP)**
**Nanoscience Foundries and Fine Analysis (NFFA- EUFP7)**

**Organizers: Lucia Reining, Ivo Souza, Stefano Fabris; R. Gebauer (Local Organiser)**

`http://cdsagenda5.ictp.it/full_display.php?agenda_id=3218`

This workshop was the 15th in a very successful series of workshops, which is held every two years at the ICTP in Trieste (Italy), and which focuses on electronic-structure methods and their applications to a steadily increasing range of materials and systems. The workshop was held on 13-15 January 2011, attracted 244 participants and consisted of 5 half-days sessions divided in 8 thematic symposia, each of which consisted of oral talks by invitation only (28 invited speakers). In addition, the program included two vibrant poster sessions (more than 150 poster presentations).

The main thematic sessions of the 15th edition included:

- Topological insulators
- Theoretical Spectroscopy
- Methodological Developments
- Pressure and temperature effects
- Materials
- Functionals and Electron correlation
- Speeding up GW and BSE
- Thermal and electronic transport.

There was a special session in the evening of January 13 to honor the upcoming 60th birthday of Matthias Scheffler (Fritz Haber Institut, MPI, Berlin) to recognize his important contributions to the electronic structure community, particularly in the field of computational heterogeneous catalysis and its application to the study of processes and systems in real working conditions. To mark this event, Prof. Klaus Kern, from the Max Planck Institute fuer Festkoerperforschung - Stuttgart, was invited to present a keynote talk on 'Surfaces in and out of equilibrium', in which he highlighted some of the outstanding contributions from Matthias Scheffler.

Oral talks were given in the Main Lecture Hall of the Leonardo da Vinci Building as in past years, while the two poster sessions were held at the Lower Level of the Adriatico Guest House. A buffet was served during these poster sessions. Posters were organized and arranged by topic. On 13 January the following topics were presented: Quantum Monte Carlo, Response to External Fields, Electronic Transport, Time Dependent Density Functional Theory, DFT beyond LDA, Many body methods in real materials, Nanoscience, Computational spectroscopies, Magnetism and Spintronics. On the following day, the topics were: Large-scale simulations, Materials design, Ab-initio molecular dynamics, Surface science, Chemical reactions and kinetics, Catalysis and electrochemistry, Functional materials, Simulations in realistic environments, and Geophysics.

The workshop was cosponsored by the International Center for Theoretical Physics (ICTP), the International School for Advanced Studies (SISSA), the CNR-IOM DEMOCRITOS Simulation Center, the Centre Européen de Calcul Atomique et Moléculaire (CECAM), the Asia Pacific Center for Theoretical Physics (APCTP) and the EU-FP7 project Nanoscience Foundries and Fine Analysis (NFFA). The Psi-k contribution was mostly used to support the travel and accommodation of young invited EU speakers/participants from the Psi-k community. This support was critical for the success of the workshop. The organizers and participants warmly thank all the institutions that supported the workshop.

## Programme

| | **Thursday, 13 January 2011** |
|---|---|
| 8:00 | Registration and administrative formalities |
| 8:50 | Organizing Committee Introduction and opening comments |
| | **SESSION 1: Topological insulators** |
| 9:00 | *Topological insulators: overview and interface/nanostructure effects*<br>Joel Moore / University of California, Berkeley, USA |
| 9:30 | *Orbital magnetoelectric effects and topological insulators*<br>David Vanderbilt / Rutgers State University of New Jersey, Piscataway, USA |
| 10:00 | Coffee Break + Registration |

| | **SESSION 2: Theoretical spectroscopy** |
|---|---|
| 10:30 | *Many-body effects in photo-emission spectra: The role of electron-phonon coupling*<br>Claudia Ambrosch-Draxl / University of Leoben, Leoben, Austria |
| 11:00 | *Auger recombination and absorption loss processes in nitride light emitters from first principles*<br>Emmanouil Kioupakis / University of California, Santa Barbara, USA |
| 11:30 | *Calculations of optical spectra from the UV-Vis to X-rays*<br>John Rehr / University of Washington, Seattle, USA |
| 12:00 | Lunch break |

| | **SESSION 3: Methodological developments** |
|---|---|
| 14:00 | *Exact factorization of the time-dependent electron-nuclear wavefunction*<br>Eberhard K.U. Gross / Max Planck Institute of Microstructure Physics, Halle, Germany |
| 14:30 | *A perspective on density matrix functional theory for ground state and excited state energy surfaces*<br>Evert J. Baerends / VU University, Amsterdam, Netherlands |
| 15:00 | *Towards accurate modeling of van der Waals interactions in complex materials*<br>Alexandre Tkatchenko / Fritz Haber Institut, Berlin, Germany |
| 15:30 | Coffee Break + Registration |
| 16:00 | *Stochastic thermostats in classical and ab initio molecular dynamics*<br>Giovanni Bussi / Istituto Nanoscienze CNR, Modena, Italy |
| 16:30 | *Computational study of optical and structural properties of an organic dye sensitized solar cell*<br>Ralph Gebauer / ICTP, Trieste, Italy |
| 17:00 | *Harnessing the power of new computer hardware for electronic structure calculations with the BigDFT code*<br>Stefan Goedecker / University of Basel, Basel, Switzerland |
| 17:30 | *NFFA Distributed Research Infrastructure for Nanoscience: Experimental and Theory Laboratories*<br>Giorgio Rossi / Laboratorio Nazionale T.A.S.C.- CNR IOM, Trieste, Italy |

| | **POSTER SESSION 1** |
|---|---|
| 17:30 | Poster setup |
| 19:00 | Poster session / free discussions |

| | **Friday, 14 January 2011** |
|---|---|

| | **SESSION 4: Pressure and temperature effects** |
|---|---|
| 9:00 | *Mott Transition in MnO and Valence Transition in Yb under Pressure: Critical Overview of an All- Electron LDA+DMFT Implementation*<br>Warren Pickett / University of California, Davis, USA |

| | |
|---|---|
| 9:30 | *Self-consistent ab-initio lattice dynamics (SCAILD); theory and numerical examples*<br>Petros Souvatzis / Uppsala University, Uppsala, Sweden |
| 10:40 | *Crystal structure prediction via particle swarm optimization: principles and applications*<br>Ma Yanming / State Key Laboratory of Superhard Materials, Changchun, P.R. China |
| 10:30 | Coffee Break<br>**SESSION 5: Materials** |
| 11:00 | *Multiferroics: Electronic degrees of freedom at play*<br>Silvia Picozzi / Consiglio Nazionale delle Richerche, CNR-SPIN L'Aquila, Italy |
| 11:30 | *Simulations of phase change materials: Order-disorder phase transitions in nanoseconds*<br>Robert O. Jones / Forschungszentrum Jlich, IFF, Jlich, Germany |
| 12:00 | Lunch break |
| | **SESSION 6: Functionals, electron correlations** |
| 14:00 | *Total energies from diagrammatic techniques: RPA, MP2 and coupled cluster*<br>Georg Kresse / Centre for Computational Materials Physics, Vienna, Austria |
| 14:30 | *Filling gaps in our understanding of gaps*<br>Klaus Capelle / Universidade Federal do ABC, Santo Andr, Brazil |
| 15:00 | *Charge transfer and other challenges in TDDFT*<br>Neepa Maitra / City University of New York, USA |
| 15:30 | Coffee Break |
| | **SESSION 7: Materials 2** |
| 16:00 | *Towards catalysis informatics*<br>Thomas Bligaard / Technical University of Denmark, Lyngby, Denmark |
| 16:30 | *Modeling dislocations and grain boundaries in graphene*<br>Oleg Yazyev / University of California, Berkeley, USA |
| | **SESSION in honour of Matthias Scheffler** |
| 17:00 | *Introduction of Keynote Speaker* |
| 17:10 | *Keynote talk: Surfaces in and out of equilibrium*<br>Klaus Kern / Max-Planck Institut fr Festkorperforschung, Stuttgart, Germany |
| 18:00 | *Remarks and informal birthday session*<br>Matthias Scheffler / Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Germany |
| | **POSTER SESSION 2** |
| 17:30<br>19:00 | Poster setup<br>Poster session / free discussions |

|  | **Saturday, 15 January 2011** |
|---|---|
|  | **SESSION 8: Speeding up GW and BSE** |
| 9:00 | *Ab initio calculations of electronic excitations: collapsing spectral sums*<br>Jan A. Berger / Ecole Polytechnique, Palaiseau, France |
| 9:20 | *GW quasi-particle spectra from occupied states only: application to DNA*<br>Paolo Umari / CNR INFM Democritos, Trieste, Italy |
| 9:40 | *GW calculations for solar energy materials using the self-consistent Sternheimer equation*<br>Feliciano Giustino / University of Oxford, Oxford, UK |
| 10:00 | *Bethe-Salpeter equation without empty electronic states applied to charge-transfer excitations*<br>Dario Rocca / University of California, Davis, USA |
| 10:20 | *Discussion* |
| 10:30 | Coffee Break<br>**SESSION 9: Thermal and electronics transport** |
| 11:00 | *Phonon transport of carbon nanotubes in ballistic, diffusive and localized regimes*<br>Takahiro Yamamoto / University of Tokyo, Tokyo, Japan |
| 11:30 | *Dynamical Coulomb blockade and the derivative discontinuity: a not-so-steady state*<br>Stefan Kurth / 1.University of the Basque Country 2.IKERBASQUE, Bilbao |
| 12:00 | *Transport in graphene nanostructures*<br>Duan Wenhui / Tsinghua University, Beijing, P.R. China |
| 12:30 | *Closing remarks* |

The full list of participants and the abstracts of the presentations at this workshop can be downloaded from the conference website or from the Psi-k portal.

### 2.1.4 Report on Cat1P: The Psi-k/CECAM research conference on Catalysis from 1st Principles

**Place:**
**Magleås Conference Center, Denmark**
**Date:**
**May 22-26, 2011**
**Sponsors:**
**Psi-k, CECAM, CAMD, Technical University of Denmark**
**Scientific Organizers:**
**Thomas Bligaard, Technical University of Denmark, Karsten Reuter, Technical University Munich, Jürgen Hafner, University of Vienna, Matthias Scheffler, Fritz-Haber-Institute, Berlin, and Jens K. Nørskov, Stanford University**
**Administrative Organizer:**
**Marianne Ærsøe, Head of Administration**
**Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark**
**Web-page:**
**http://www.cecam.org/workshop-0-569.html**

**In brief:**

The Psi-k and CECAM joint research conference: Catalysis from 1st Principles was held May 22-26, 2011 at the Magleås Conference Center in Northern Sjælland in Denmark. Thanks to the 53 participants the conference there was a lively discussion at the conference, which primarily focused on the topics relating to challenges for the design of catalytic materials by first principles simulations. The conference was the 7th in the Cat1P - Catalysis from first Principles series that have been arranged by Matthias Scheffler, Jürgen Hafner, Jens Nørskov and colleagues. The meeting thus followed workshops in Magleås, Denmark (1999 and 2004), CECAM Lyon (2000 and 2006), and Vienna (2002 and 2009). It was also inspired by the series of 1998, 2007, and 2009 Psi-k workshops entitled Theory meets industry which were organized by Jürgen Hafner and colleagues. This conference was held as a European Gordon-type conference in an isolated site with natural surroundings with exclusively posters and invited talks, afternoons off, and a relatively long time scheduled for discussions around each talk.

**Motivation:**

Quantum theoretical calculations of extended atomic- scale systems have reached a level of speed and accuracy that allows determining many interesting materials properties directly from simulations. This gives unprecedented possibilities for addressing materials design problems from a bottom-up approach, where theoretical simulations and concepts derived from such simulations are used directly to propose new materials for subsequent experimental synthesis and testing. Solid surfaces are used extensively as catalysts in the chemical and energy industry and the development of new approaches to discovering catalysts with high efficiency, activity, stability, and selectivity are essential.

**Objectives and scientific report:**

The aim of the meeting was be to bring together researchers who characterize and design technical catalysts in industry, with experimental catalysis researchers, researchers who carry out computer simulations on catalytic materials and reactions, theoreticians who develop methodology enabling larger and more accurate electronic structure calculations on more complex materials and molecules, method developers who are working on the development of methods for more accurate thermodynamic and kinetics sampling, and researchers working on more general aspects of atomic-scale materials design. In this forum the challenges for the design of novel catalytic materials were to be discussed.

The main objectives of the 2011 meeting were: (i) to review and discuss the current status of and future prospects for applying ab initio and statistical mechanics approaches to the study of chemical processes at solid surfaces; (ii) to discuss how calculational methods are now being used as a tool for the design of new materials in general and of heterogeneous and electrochemical catalysts in particular; (iii) to discuss recent applications and future prospects of using such approaches to understand interfaces of electrochemical and environmental importance; (iv) to discuss the possibilities for improving the present state of the art towards better describing complex compounds such as oxides and van der Waals-bonded systems; (v) to identify and analyze main obstacles for the atomic-scale simulations to be utilized more broadly as a platform for developing new catalytic materials; (vi) to inspire leading experimental researchers towards identifying which types of future experiments that could be central for synergy with the computational community in order to extend the limited existing methods for computational catalyst screening into the regime of more complex materials and compounds. All these issues were carefully addressed. Especially the roles of the atomic-scale structure at interfacial boundaries and the realistic simulation treatment of reaction conditions and their influence of structure were discussed in detail.

**Programme:**

**Sunday 22nd**

Check-in possible from 16:00
18:00-19:30 Dinner
Evening session, Chair: T. Bligaard
19:30-20:20 J.K. Nørskov
20:20-21:10 A. Michaelides

**Monday 23rd**

7:40-8:40 Breakfast

Morning session, Chair: A. Michaelides

8:40-9:30 A. Schäfer
9:30-10:20 P. Sautet
10:20-10:50 Coffee
10:50-11:40 M. Amft
11:40-12:30 T. Ziegler
12:30-13:30 Lunch
13:30-16:00 Free time
16:00-18:00 Poster Session
18:00-19:30 Dinner
Evening session, Chair: P. Sautet
19:30-20:20 S. Piccinin
20:20-21:10 J. Rossmeisl

**Tuesday 24th**

7:40-8:40 Breakfast

Morning session, Chair: J. Rossmeisl

8:40-9:30 P. Raybaud
9:30-10:20 F. Mittendorfer
10:20-10:50 Coffee
10:50-11:40 N. Lopez
11:40-12:30 K.W. Jacobsen
12:30-13:30 Lunch

13:30-16:20 Free time
Afternoon session, Chair: A. Schäfer
16:20-17:10 R. Schomcker
17:10-18:00 V. Ganduglia-Pirovano
18:00-19:30 Dinner
Evening session, Chair: P. Sautet
19:30-20:20 G. Pacchioni
20:20-21:10 M. Salmeron

**Wednesday 25th**

7:40-8:40 Breakfast

Morning session, Chair: F. Mittendorfer

8:40-9:30 K. Reuter
9:30-10:20 S. Dahl
10:20-10:50 Coffee
10:50-11:40 T. Bucko
11:40-12:30 M. Maestri
12:30-13:30 Lunch
13:30-16:20 Free time
Afternoon session, Chair: V. Ganduglia-Pirovano
16:20-17:10 S. Levchenko
17:10-18:00 B. Temel
18:00-19:30 Dinner
Evening session, Chair: N. Lopez
19:30-20:20 R. Horn
20:20-21:10 C. Dellago

**Thursday 26th**

Before 9:00 Check-out of rooms before 9:00

7:40-8:40 Breakfast

Early morning session, Chair: K. Reuter

8:40-9:30 E. Beret
9:30-10:20 B. Hammer
10:20-10:50 Coffee
Late morning session, Chair: T. Bucko
10:50-11:40 G. Jones
11:40-12:30 F. Abild-Pedersen
12:30-13:30 Lunch

List of Participants:

J.K. Nørskov, Stanford
A. Michaelides, UCL
M. Salmeron, LBNL
P. Sautet, ENS-Lyon
C. Dellago , U. Vienna
T. Ziegler, U. Calgary
S. Piccinin , CNR-IOM Democritos
J. Rossmeisl, DTU
P. Raybaud, IFP
F. Mittendorfer, TU Wien
N. Lopez, ICIQ
K.W. Jacobsen, DTU
R. Horn, FHI
R. Schomäcker, TU Berlin
G. Pacchioni, U. Milano-Bicocca
F. Abild-Pedersen, SLAC
K. Reuter, TU München
S. Dahl, CASE/DTU
T. Bucko, Comenius University
M. Maestri, Politecnico di Milani
S. Levchenko, FHI
B. Temel, Haldor Topsøe A/S
V. Ganduglia-Pirovano, I. Catal. and Petrochem., Madrid
A. Schäfer, BASF
E. Beret, FHI
B. Hammer, U. Aarhus
G. Jones, Johnson Matthey
M. Amft, U. Uppsala
T. Bligaard, SLAC
J. Wellendorff, DTU

K. Lundgd̊, DTU
H. Falsig, DTU
A. Toftelund, DTU
T. Khan, DTU
J. Howalt, DTU
V. Tripkovic, Comp. Mat. Design ApS
ZhenHua Z., DTU
M. Karamad, DTU
S. Siahrostami, DTU
N. Ammitzbøll, DTU
I. Man, DTU
L. Vilhelmsen, U. Aarhus
A. Rasmussen, U. Aarhus
H. Gao, U. Aarhus
Seung-Cheul Lee, Korea Institute of Science and Technology
C. Mangold, FHI
F. Göltl, U. Vienna
C. Ebensperger, U. Erlangen
D. Karhanek, ICIQ
K. Kwapien, Humboldt-U. Berlin
M. Petersen, Sasol
K. Andersen, DTU
M. Björketun, DTU

### 2.1.5 Report on Workshop on Dynamical Properties of Earth and Planetary Materials

**CECAM-HQ-EPFL, Lausanne, Switzerland**

**October 10, 2011 to October 13, 2011**

**Sponsors: CECAM and Psi-k**

**Organizers: Razvan CARACAS, Bjoern WINKLER and Lars STIXRUDE**

**Web Page:** `http://www.cecam.org/workshop-0-551.html`

#### Summary

The exponential development of powerful algorithms, implementations and computational power over the last decade has seen the application of first-principles calculations in solving critical problems of mineral physics expand at an unprecedented pace. Theoretical mineral spectroscopy, high-pressure thermodynamics, construction of phase diagrams, determination of melts and melting curves go hand in hand today with experimental investigations. The thermodynamic and thermochemical conditions that we are able to successfully reproduce in the computer simulations cover the entire range existent in our planet, our solar system or in other distant worlds.

Our workshop aimed at advancing exchanges among theorists using different approaches, as well as between theorists and experimentalists, in order to enhance and broaden the use of first principles calculations in geosciences. In particular we featured mini-sessions on:

- melts and glasses, with experimental contributions about the structure of silicate and borosilicate glasses at ambient pressure conditions, with atomistic simulations about the behavior of geologic fluids and melts and with first-principles molecular-dynamics approach on the state of the primordial magma ocean;

- experimental overviews, covering a wide range of topics: a infrared and raman study of the magnetic transitions in ilvaite, a synchrotron study on the diffuse scattering and its use in understanding phonon band dispersion and phase transitions, a review of the behavior of molecular solids under pressure, a study about the kinetics of a solid-solid reaction in silicates at mid-mantle conditions, a study of the elasticity of MgO, a review about the plasticity of MgO and the methods used to describe it, and a study on determining melting and thermodynamical properties of materials at ultra-high pressure using nuclear resonant inelastic x-ray scattering measurements;

- computational techniques, including advances and illustrations of the use of the SIESTA and CASTEP packages, an overview of the computation of Moessbauer and NMR spectra from ab initio calculations, and a study about the determination of infrared spectra

- iron-bearing high-pressure phases, covering computational and experimental studies of the spin transition in mantle minerals at extreme conditions, its effect on elasticity, seismic properties, thermodynamical and spectroscopic properties, as well as a detailed description and understanding of the associated structural changes

- isotope partitioning, with experimental and theoretical contributions on determining isotope partitioning between minerals and between fluids and solids, including isotopes of B, Li, Si and Fe.

**Programme**

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Day 1 - October, 10th 2011

SESSION I: Melts and Glasses

13:50 to 14:00 - Welcome

14:00 to 14:50 - Neuville Daniel
                 Structure and properties of silicate melts:
                 From volcanic activity to industrial processes

14:50 to 15:40 - Sung Keun Lee
                 Universal behavior in pressure-induced melt-polymerization
                 in silicate melts in Earth's interiors

15:40 to 16:10 - Coffee Break

16:10 to 17:00 - Lars Stixrude
                 Dynamics of silicate liquids at high pressure

17:00 to 17:50 - Sandro Jahn
                 Structure and properties of geological melts and fluids:
                 A combined experimental and computational approach


Day 2 - October, 11th 2011

SESSION II: Experimental approaches

09:00 to 09:50 - Monika Koch-Mueller
                 Pressure-induced phase transitions in Ilvaite studied
                 by In-situ Mid/Far Micro-FTIR spectroscopy

09:50 to 10:40 - Alexei Bosak
                 Diffuse scattering in simple materials: modeling and
```

interpretation

10:40 to 11:10 - Coffee Break

11:10 to 12:00 - Roberto Bini
Tuning of the electronic properties of simple model molecules by pressure and their implications in high pressure chemistry

12:00 to 14:00 - Lunch Break

14:00 to 14:50 - David Dobson
Kinetics of the reaction perovskite + ferropericlase = ringwoodite

14:50 to 15:20 - Sergio Speziale
Elastic properties of deep Earth materials by Brillouin scattering of polycrystalline materials at high pressures: The role of grain size and of texturing in MgO

15:20 to 15:50 - Coffee Break

15:50 to 16:40 - Cordier Patrick
Modeling plastic deformation of MgO under mantle conditions

16:40 to 17:30 - Jennifer Jackson
Melting behavior and phonon measurements of earth materials above 1 megabar

Day 3 - October, 12th 2011

SESSION III: Advances in computational techniques

08:30 to 09:20 - Alberto Garcia
New and forthcoming functionalities in the SIESTA code

09:20 to 10:10 - Josef Zwanziger
Computational Approaches to Moessbauer and Magnetic Resonance Spectroscopies

10:10 to 10:30 - Coffee Break

10:30 to 11:20 - Keith Refson
Vibrational spectroscopy with the CASTEP code

11:20 to 12:30 - Marc Blanchart
Infrared spectroscopy of minerals from first-principles

SESSION IV: Iron-bearing high-pressure phases

14:00 to 14:50 - Jung-Fu Lin
Electronic and Elastic Properties of Iron-Containing
Minerals in Earth's Interior

14:50 to 16:40 - Stuart Gilder
Magnetic properties of iron and iron-bearing phases
at high pressure

16:40 to 17:00 - Coffee Break

17:00 to 17:50 - Razvan Caracas
Spin transition in Fe-bearing perovksite

17:50 to 18:40 - Boffa Ballaran Tiziana
Effect of Fe and Al substitution on the elastic properties
of perovskite: a single-crystal diffraction study up to 75 GPa.

19:30 to 22:30 - Dinner

Day 4 - October, 13th 2011

SESSION V: Isotope partitioning

09:00 to 09:50 - Mathieu Roskosz
Experimental and spectroscopic approach to the determination
of equilibrium Fe isotopic fractionation factors in planetary
materials

09:50 to 10:40 - Piotr Kowalski
First principles calculation of B and Li equilibrium isotope
fractionation between minerals and aqueous solutions

10:40 to 11:10 - Coffee Break

`11:10 to 12:00 - Merlin Meheut`
`The structural determinants of silicon fractionation properties of silicate minerals : a First-Principles Density Functional Study`

**List of participants**

Organizers

Caracas Razvan - CNRS-Laboratory of Earth Sciences, Ecole Normale Superieure Lyon, France
Stixrude Lars - University College London, United Kingdom
Winkler Bjoern - Johann Wolfgang Goethe University, Frankfurt, Germany

Participants

Bini Roberto - University Florence, Italy
Blanchart Marc - Institut de Mineralogie et de Physique des Milieux Consenses (IMPMC), Paris , France
Bosak Alexei - European Synchrotron Radiation Facility (ESRF), Grenoble, France
Daniel Neuville - CNRS-Institut de Physique du Globe de Paris, France
Dobson David - University College London, United Kingdom
Garcia Alberto - Institute of Materials Science, Barcelona, Spain
Gilder Stuart - Ludwig Maximilians University, Munich, Germany
Jackson Jennifer - Caltech, Pasadena, USA
Jahn Sandro - German Research Centre for Geosciences, Potsdam, Germany
Koch-Mueller Monika - German Research Centre for Geosciences, Potsdam, Germany
Kowalski Piotr - Helmholtz Centre Potsdam, Germany
Lee Sung Keun - Seoul National University, South Korea
Lin Jung-Fu - University of Texas, Austin, USA
Meheut Merlin - CNRS-Institut de Mineralogie et de Physique des Milieux Condenses (IMPMC), Paris, France
Patrick Cordier - Universite Lille 1, France
Refson Keith - Rutherford-Appleton Laboratory, United Kingdom
Roskosz Mathieu - Univ. Lille 1, France
Speziale Sergio - German Research Centre for Geosciences, Potsdam, Germany
Tiziana Boffa Ballaran - University Bayreuth, Germany
Zwanziger Josef - Dalhousie University, Halifax, Canada

### 2.1.6 Report on Workshop ”Perspectives and challenges of many-particle methods: efficient strategies and tools for describing complex systems

| | |
|---|---|
| Organizers: | Prof. Dr. Thomas Frauenheim, University Bremen, BCCMS, Germany<br>Prof. Dr. Alexander Lichtenstein, University of Hamburg, Germany<br>Prof. Dr. Christian Ochsenfeld, Technical University Munich, Germany<br>Prof. Dr. Andreas Savin, University Pierre Marie Curie, Paris, France |
| Location: | University of Bremen, Germany,<br>19.-23. September 2011 |

**Summary**

The workshop Perspectives and challenges of many- particle methods: efficient strategies and tools for describing complex systems was held at the University of Bremen, Germany from September 19th to 23rd 2011. In total, 78 participants from Austria, China; France, Germany, Israel, Italy, The Netherlands, Norway, Russia, Spain, USA, UK, Denmark, Japan, Sweden, Switzerland attended the workshop.

The programme consisted of 30 invited lectures, one poster session presenting 32 posters and many events (reception / conference dinner) to allow for informal exchange. The lectures were scheduled to last 40 min, including 5-10 min discussion time. In addition to this extended time for discussion, the chairpersons were instructed to introduce the subject of the session and to actively participate in the discussion. This Gordon-conference-style was essential to guarantee a vivid discussion. The organizers ensured that well-established scientists acted as invited speakers and chairpersons.

Concerning the poster session, we accepted only 32 posters to allow for an intense exchange of ideas at each single poster. Here, we encouraged in particular the young scientists to ask questions. The participation of PhD students was supported by partly covering local accommodation costs.

Due to the compact organization and accommodation in one hotel only all participants had to stay together for the whole time of the conference, which additionally enforced the scientific discussion which was mandatory since scientists from various separated fields, i.e. advanced quantum chemistry, quantum Monte-Carlo, many-body perturbation theory, time-dependent DFT, etc. were attending the meeting to merge ideas and formulate a common goal for future method developments.

Financial support from the European Science Foundation (ESF), Psi-k Charity, the German CECAM node multiscale modelling from first principles, cecam-mm1p.de and the University Bremen is gratefully acknowledged.

## Scientific content and discussion

The field of computational material science made recently a tremendous step toward a first-principle description of correlated electronic systems including transition metal and rare-earth elements. A great impact is expected in the new area of artificially constructed magnetic nano-systems and at the interface of traditional inorganic chemistry, physics, biology and materials science in general. Of prime importance is the development of next-generation realistic many-body computational tools which are fast, reliable and are able to describe non-trivial quantum dynamics of complex systems. In order to address these problems, new integrated software tools for realistic quantum simulations of correlated systems need to be developed for a broad scientific community.

Recently a new generation of continuous-time Quantum Monte Carlo (CT-QMC) methods for numerically exact calculation of complicated fermionic path integrals have been proposed for interacting electrons based on the weak-coupling and strong-coupling perturbation expansion. This methodological breakthrough in the quantum many-body theory stimulate a great progress in the electronic calculations of realistic and increasingly complex strongly correlated systems within the dynamical mean-field theory (DMFT) where the solution of effective multiband impurity problem is the main point. New QMC technique stimulate the fast and important developments in the field of strongly correlated materials related with the realistic LDA+DMFT calculations for the d- and f-orbital cases, heavy-fermion systems, strongly correlated thermoelectric compounds and novel high-temperature superconducting pnictides.

Over the past decades, density functional theory (DFT) has become the effective single-particle theory of choice both for physicists from the solid state community as well as for quantum chemists. However, this tremendous success is also accompanied by an ever growing list of documented failures, especially for strongly correlated systems. Modern approaches to improve the description by better exchange-correlation functionals are based on an adapted treatment for short and long-range electron-electron interaction (so called range-seperated functionals) or the seperate treatment of exchange and correlation functionals (exact exchange + random phase approximation).

Beyond DFT, the GW/BSE approximations based on MBPT have found widespread use in the calculation of single-particle spectra. Originally used only to compute band structures in solids, GW has recently also been applied to study surfaces and molecules. A detailed comparison of the self energy in the GW context with the exchange-correlation functional in DFT, is expected to pave the road for further improvement of functionals. This interplay of different approaches to correlated systems was already exploited in the realm of time dependent DFT.

Yet other approaches for interacting many-electron systems were put forward in the quantum chemistry community. Wavefunction-based schemes allow to systematically approach the exact solution of the electronic Schroedinger equation and in this way offer a hierarchy useful for estimating error bars of simpler approximations. The methods range from efficient MBPT methods mostly employing Gauss-type basis functions to coupled-cluster theory and also multi-reference approaches. To deal with the cusp problem and basis deficiencies, r12 and more recently F12 methods have been brought forward. The steep increase of the computational effort with molecular size has been circumvented by introducing linear-scaling methods for many quantum-chemical methods and for computing various molecular properties. They exploit the local electronic structure and open the way to treat large molecular systems with 1000 atoms and more at the HF, DFT, and MP2 levels. Also the possibilities in performing highly accurate CC calculations has been dramatically increased. Finally, also partially periodic boundary conditions have been accounted for. The relation of all of these schemes to the correlated methods in the many-body physics community is just now starting to be on a systematic level.

An interesting first-principle alternative to LDA+U scheme for correlated materials is related with developments of Reduced-density-matrix-functional theory (RDMFT). It is based on old Gilberts theorem, which shows that the expectation value of any observable in the ground state can be expressed as a functional of the one-body reduced density matrix. The advantage of RDMFT approach, compared to DFT, is that the exact many-body kinetic energy is easily expressed in terms of reduced-density-matrix. The RDMFT calculations of transition metal oxides gives correct insulating states of these correlated compounds.

The variety of approaches show the zoo of methods to tackle the highly complex many-body problem. Although there are many links between the methods, it is often highly difficult to find unifying features. The very lively discussions in the workshop clear showed the different languages, but also the many common features in aiming for the ultimate goal of solving the many body problem, which made the workshop a full success.

While density-functional being in principle exact, the lectures clearly showed the many difficulties in developing better functionals and to step up Perdew's advocated Jacob's ladder.

Another central problem clearly appearing in several talks is not only the treatment of dynamic correlation, but also of static correlation. While many attempts have been and are made, the path towards cost-efficient and highly accurate schemes is still a major challenge. A brute force scheme often used as a reference is certainly QMC, however, the difficulty of a statistical method and the systematic error control at realistic costs is clear. In particular the lack of error cancellation in relative energies remains a drawback. Nevertheless, the importance of reliable benchmarks is always present and here QMC and CC methods are central to calibrate and understand simpler approximations to the many-body problem. The developments made in these areas presented in several lectures are highly impressive.

Also the field of basis expansions remains a challenge: in plane-wave codes the use of ECP remains an issue, while in Gaussian-type basis sets the influence of basis deficiencies and basis-set superposition errors (both inter- and intra-molecular BSSE) plays a major role. For the latter so-called F12 methods for describing the cusp have shown major improvements During the workshop there were many important discussions on the challenges and future directions of realistic many-body methods for electronic structure calculations. After the talk of Prof. S. Louie on GW-approach the ultimate limit for the size of simulation system in the present GW-program and in the future approach have been discussed. The question of possibility to investigate the dipole-forbidden d-d transitions in optical spectrum of NiO within the Bethe-Salpeter (BS) equation was discussed after the talk by Prof. F. Bechstedt. It was pointed out that the first-principle investigations of optical spectra for strongly correlated oxides will be possible in the near future. Possible collaborations with the DMFT-community on the problem of vertex-corrections in optical spectrum of correlated oxides will be very useful for the GW-community.

The talk by Prof. S. Biermann on the DMFT extension to GW scheme have been generated a discussion on the progress of QMC calculations with screened Coulomb interactions. It was pointed out that if numerically exact solution of the local quantum impurity problem with frequency dependent interactions is possible for multiorbital d- and f- systems, then one can efficiently combined the GW+DMFT scheme to treat correlation effects in transition metal and rare-earth materials. In this case the new possibilities is open in the research on new class of Fe-based high-temperature superconductors, were both non-local spin-fluctuation effects and local Coulomb correlations are important for understanding the mechanism of non-convention electron pairing phenomena.

During the session on DFT+DMFT (Profs. V. Rubtsov, K. Held and M.R. Valenti) an important question on the accuracy of continuous-time QMC scheme for realistic heterostructure and cluster calculations have been discussed. Different aspects of the interaction- and hybridization-expansion CT-QMC methods for multiorbital correlated impurity problems was analyzed. The development of the optimal CT-QMC solver will be an important task for the DMFT-community in future.

A discussion on the future of many-body perturbation scheme for a finite quantum systems, after the talk by Prof. M. Scheffler, was very useful for future of GW, CC and other methods. Moreover, the similar discussion (Prof. G. Kresse) on the quality of self-consistent GW scheme which include not only the direct, but also the exchange second-order, in the screened Coulomb potential, contribution to the total energy, shows a very good agreement with an accurate CC-results. This can be of crucial importance for the future approach to the many-body perturbation scheme for realistic correlated systems and also shows an creative collaboration between physics and quantum-chemistry communities.

### Assessment of the results and impact on future direction of the field

With its focus on many-body methods, the workshop brought together researchers from a wide variety of different backgrounds and very different 'scientific languages'. Although there are many common features, the complexity of the methods makes it often very difficult to find more useful links and in this way to approach better solutions to the many-body problem which is of central importance. Therefore many more meetings of this kind are highly desirable and can help to find better approaches that allow to describe materials - and complex systems in general - in a much more accurate and efficient way. Therefore, a follow-up workshopsevery two or three years would be desirable.

The objectives of the workshop have been fully achieved. The workshop became a forum to brainstorm ideas about solutions to important correlated-electrons problems and identify new directions for many-body method development and challenging applications. There is ongoing intensive exchange of benchmark data between the many-body physics and the correlated quantum chemistry community while both communities are approaching applications to more complex and larger realistic systems.

The most advanced computational methods nowadays achieve a predictive level close to experimental data of materials properties and functions. In analysing this, there is a paradigm change. Computational applications are not anymore aiming only at interpreting experimental results but rather predict new materials systems and devices. The delivery of this new computational technology to a broad community in future will facilitate breakthroughs on high-impact materials science problems in nano-science, biophysics and new energy storage.

There are lots of ongoing discussions between the different development directions (QMC, MBPT in quantum chemistry and physics, development of new functional, etc.), (though competition) even close intense collaborations for validating the methods against each other and pushing the field to the limits of quantitative accuracy.

## Invited Speaker and Chairperson

| | |
|---|---|
| Prof. Dr. Roi Baer | The Hebrew University of Jerusalem, Israel |
| Prof. Dr. Friedhelm Bechstedt | University of Jena, Germany |
| Prof. Dr. Silke Biermann | École Polytechnique Palaiseau, France |
| Prof. Dr. Peter E. Bloechl | Clausthal University of Technology, Germany |
| Prof. Dr. Guanhua Chen | The University of Hong Kong |
| Dr. Henk Eshuis | University of California, US |
| Prof. Dr. Thomas Frauenheim | University of Bremen, Germany |
| Prof. Dr. Andreas Goerling | University of Erlangen-Nuremberg, Germany |
| Prof. Dr. Eberhard K. U. Gross | Max Planck Institute Halle, Germany |
| Prof. Dr. Martin P. Head-Gordon | University of California, Berkeley, US |
| Prof. Dr. Karsten Held | Vienna University of Technology, Austria |
| Prof. Dr. Trygve Helgaker | University of Oslo, Norway |
| Prof. Dr. Carmen Herrmann | University of Hamburg, Norway |
| Prof. Dr. Mikhail Katsnelson | Radboud University, Nijmegen, Netherlands |
| Prof. Dr. Erik Koch | FZ-Juelich, Germany |
| Prof. Dr. Georg Kresse | University of Vienna, Germany |
| Prof. Dr. Alexander Lichtenstein | University of Hamburg, Germany |
| Prof. Dr. Steven G. Louie | University of California, Berkeley, US |
| Dr. Tim Mueller | Massachusetts Institute of Technology, Boston, US |
| Prof. Dr. Frank Neese | Max Planck Institute for Bioinorganic Chemistry, Muelheim |
| Prof. Dr. Christian Ochsenfeld | University of Munich, Germany |
| Dr. Lucia Reining | École Polytechnique, Paleissau, France |
| Dr. César Rodríguez-Rosario | University of Bremen, Germany |
| Prof. Dr. Michael Rohlfing | University of Osnabrueck, Germany |
| Prof. Dr. Angel Rubio | University of the Basque Country, San Sebastian, Spain |
| Prof. Dr. Giovanni Onida | University of Milan, Italy |
| Prof. Dr. Alexey Rubtsov | Moscow State University, Russia |
| Prof. Dr. Peter Saalfrank | University of Potsdam, Germany |
| Prof. Dr. Andreas Savin | CNRS and UPMC, Paris, France |
| Prof. Dr. Matthias Scheffler | Fritz-Haber-Institut, Berlin, Gemany |
| Prof. Dr. Martin Schuetz | University of Regensburg, Germany |
| Prof. Dr. Gustavo E. Scuseria | Rice University, Houston, US |
| Prof. Dr. Hans-Joachim Werner | University of Stuttgart, Germany |
| Dr. Weitao Yang | Duke University, Durham, US |
| Prof. Dr. Maria-Roser Valenti | Goethe University of Frankfurt, Germany |

## Participants

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|---|---|
| Dr. János ngyán | Nancy University, France |
| Dr. Bálint Aradi | University of Bremen, Germany |
| Moloud Kaviani Baghbadorani | University of Bremen, Germany |
| Matthias Beer | University of Munich, Germany |
| Lucien Clin | University of Munich, Germany |
| Prof. Dr. Gerd Czycholl | University of Bremen, Germany |
| Dr. Andreia Luisa da Rosa | University of Bremen, Germany |
| Dr. Peter Deák | University of Bremen, Germany |
| Dr. Grygoriy Dolgonos | University of Bremen, Germany |
| Ireneusz W. Bulik | Rice University, Houston, US |
| Francesco Calcavecchia | University of Mainz, Germany |
| Dr. Javier Daniel Fuhr | Atomic Center Balseiro Institute, San Carlos de Bariloche, Argentinia |
| Dr. Ádám Gali | Hungarian Academy of Sciences, Budapest, Hungary |
| Fabio Caruso | Fritz Haber Institute, Berlin, Germany |
| Dr. Andreas Gruneis | University of Cambridge, UK |
| Vamshi Mohan Katukuri | Dresden University of Technology, Germany |
| Andris Gulans Aalto | University COMP Espoo, Finland |
| Dr. Jiri Klimes | University College London, UK |
| Matteo Guzzo | École Polytechnique Laboratoire des Solides Irradiés Palaiseau, France |
| Dr. Gerald Knizia | Cornell University, Ithaca, NY, US |
| Atefeh Hassnieh | University of Manchester, UK |
| Thomas Koehler | University of Bremen, Germany |
| Dr. Andreas Hesselmann | University of Erlangen-Nuremberg, Germany |
| Dr. Joerg Kussmann | University of Munich, Germany |
| Dr. David Jacob | Max Planck Institute of Microstructure Physics Halle, Germany |
| Marc Landmann | University of Paderborn, Germany |
| Harald O. Jeschke | Goethe University of Frankfurt, Germany |
| Dr. Hunpyo Lee | Goethe University of, Germany |
| Merzuk Kaltak | University of Vienna, Austria |
| Dr. Gang Li | University of Wuerzburg, Germany |
| Martina Maurer | University of Munich Munich, Germany |
| Matthieu Saubanere | University of Kassel, Germany |
| Simon Maurer | University of Munich, Germany |
| Dr. Vinit Sharma | University of Witwatersrand Johannesburg, South Africa |
| Tobias Mueller | University of Kassel, Germany |
| James J. Shepherd | University of Cambridge, UK |
| Dr. Singh Nirpendra | King Abdullah University of Science and Technology Thuwal, Kingdom of Saudi Arabia |
| Dr. Ronald Starke | University of Vienna Vienna, Austria |

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|---|---|
| Ari Ojanperae Aalto | University Espoo, Finland |
| Tamar Stein | The Hebrew University of Jerusalem, Israel |
| Dr. Rossitza Pentcheva | University of Munich, Germany |
| Marcus Turowski | Laser Center Hannover, Germany |
| Dr. Alexander N. Rudenko | Hamburg University of Technology, Germany |
| Marton Voros | Budapest University of Technology and Economics, Hungary |
| Dr. Ersoy Sasioglu | Juelich Research Center, Germany |
| Dr. Yong Xu | Fritz Haber Institute Berlin, Germany |
| Dr. Binghai Yan | University of Bremen, Germany |

## Programme

**Monday, September 19th 2011**(Ramada Ueberseehotel Bremen)

**18:00-21:00** **Registration**

**Tuesday, September 20th 2011** (The Sparkasse Bremen/Downtown Am Brill 1)

**08:00-08:50** **Registration**

**08:50-09:00** **Opening and welcome**, Thomas Frauenheim

**Session: GW and beyond**

**Chair: Martin Head-Gordon**

**09:00-09:40** Steven G. Louie, University of California, Berkeley (US)
Role of many-particle effects in determining experimentally observed properties: The GW approach

**09:40-10:20** Michael Rohlfing, University of Osnabrueck (Germany)
Many-body perturbation theory for large systems: An LDA+GDW approach

**10:20-11:00** Friedhelm Bechstedt, University of Jena (Germany)
Many-body perturbation theory for bands, excitons and optical spectra of magnetic insulators

**11:00-11:30** **Coffee Break**

**Session:DFT+DMFT (I)**

**Chair: Thomas Frauenheim**

**11:30-12:10** Silke Biermann, École Polytechnique, Paris (France)
Dynamical Mean-Field Theory (DMFT) and its extensions: First principles calculations for correlated materials

**12:10-12:50** Mikhail Katsnelson, Radboud University of Nijmegen (The Netherlands)
Itinerant electron magnetism

**12:50-15:00** **Lunch Break and Coffee**

**Session: DFT+DMFT (II)**

**Chair: Andreas Savin**

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|---|---|
| **15:00-15:40** | Alexey Rubtsov, Moscow State University (Russia)<br>Dual variables for correlated systems with collective modes |
| **15:40-16:20** | Karsten Held, Vienna University of Technology (Austria)<br>LDA+DMFT: From bulk to heterostructures |
| **16:20-17:00** | Maria-Roser Valenti, Goethe University of Frankfurt (Germany)<br>LDA+DMFT for the new Fe-based superconductors |
| **19:00-21:30** | **Welcome Reception** (Bremen Town Hall) |

**Wednesday, September 21$^{st}$ 2011** (The Sparkasse Bremen/Downtown Am Brill 1)

**Session: QMC and RDMFT (I)**

**Chair: Steven G. Louie**

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| **09:00-09:40** | Tim Mueller, Massachusetts Institute of Technology (US)<br>Quantum Monte Carlo for materials design |
| **09:40-10:20** | Erik Koch, Research Centre Juelich (Germany)<br>Building realistic models of correlated materials |
| **10:20-11:00** | Matthias Scheffler, Fritz Haber Institute of the Max Planck Society (Germany)<br>The random phase approximation for the electron correlation energy and beyond |
| **11:00-11:30** | **Coffee Break** |

**Session:QMC and RDMFT (II)**

**Chair: Weitao Yang**

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|---|---|
| **11:30-12:10** | Peter E. Bloechl, Clausthal University of Technology (Germany)<br>Density-matrix-functional theory as a bridge between DFT and explicit many-particle theory |
| **12:10-12:50** | Gustavo Scuseria, Rice University Houston, Texas (US)<br>Symmetry breaking, restoration and density matrix functional theory |
| **12:50-14:30** | **Lunch Break** |
| **14:30-15:10** | Martin P. Head-Gordon, University of California, Berkeley (US)<br>Simple wave functions for strong electron correlations |

**Session: MBPT and CC-approach (I)**

**Chair: Eberhard K. U. Gross**

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| **15:10-15:50** | Martin Schuetz, University of Regensburg (Germany)<br>Local correlation methods for excited state calculations of extended systems |
| **15:50-16:20** | **Coffee Break** |
| **16:20-17:00** | César A. Rodríguez-Rosario, University of Bremen (Germany)<br>Open quantum systems TD-DFT: Fundamental theorems |
| **17:00-17:40** | Peter Saalfrank, University of Potsdam (Germany)<br>Correlated wavefunction methods for electron dynamics |
| **19:00-23:00** | **Conference Dinner** (Juergenshof Bremen) |

**Thursday, September 22nd 2011** (BCCMS University Campus, TAB Building)

**Session: MBPT and CC-approach (II)**
**Chair: Alexander Lichtenstein**

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| **09:00-09:40** | Frank Neese, University of Bonn (Germany)<br>Efficient wavefunction based single and multi-reference ab initio methods for larger molecules |
| **09:40-10:20** | Hans-Joachim Werner, University of Stuttgart (Germany)<br>Explicitly correlated coupled-cluster and multi-reference correlation methods |
| **10:20-10:50** | **Coffee Break** |

**Session: DFT-Hybrid, RPA and beyond (I)**
**Chair: Martin Schuetz**

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|---|---|
| **10:50-11:30** | Georg Kresse, University of Vienna (Austria)<br>Explicitly correlated ground state calculations for solids RPA and CCSD |
| **11:30-12:10** | Henk Eshuis, University of California, Irvine (US)<br>Efficient evaluation of RPA correlation energies with applications to non-covalent interactions and reaction energies |
| **12:10-12:50** | Eberhard K. U. Gross, Max Planck Institute of Microstructure Physics, Halle (Germany)<br>Density-matrix functional theory of strongly correlated solids |
| **12:50-15:00** | **Lunch Break and Coffee** |

**Session: DFT-Hybrid, RPA and beyond (II)**
**Chair: Carmen Herrmann**

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|---|---|
| **15:00-15:40** | Roi Baer, The Hebrew University of Jerusalem (Israel)<br>Tuned range separated hybrids: Fundamental gaps and excitation energies of finite systems from a single generalized Kohn-Sham framework |
| **15:40-16:20** | Trygve Helgaker, University of Oslo (Norway)<br>Molecular electronic structure in strong magnetic fields |
| **16:20-17:00** | Weitao Yang, Duke University, Durham (US)<br>Extension of approximate density functionals and many-electron theories to fractional charges and fractional spins |
| **17:30-21:30** | **Poster Session** & Buffet (Catering Service) |

**Friday, September 23rd 2011** (BCCMS University Campus, TAB Building)

**Session: TD-DFT+MBPT**
**Chair: Christian Ochsenfeld**

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| **09:00-09:40** | Andreas Goerling, University of Erlangen (Germany)<br>Density functionals for the correlation energy within the random phase approximation |

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| **09:40-10:20** | Lucia Reining, cole Polytechnique, Palaiseau (France)<br>Fingerprints of correlation in electronic spectra - beyond the quasiparticle approximation |
| **10:20-11:00** | Giovanni Onida, University of Milano (Italy)<br>Optical properties of complex and realistic systems: A challenge for theories and codes |
| **11:00-11:30** | **Coffee Break** |
| **11:30-12:10** | Angel Rubio, University of the Basque Country,<br>San Sebastian (Spain)<br>First principlesmodeling of nanostructured-based devices:<br>From photovoltaics to light-emission |
| **12:10-12:50** | Guanhua Chen, University of Hong Kong (China)<br>Time-dependent density-functional theory for open systems |
| **12:50-13:00** | **Closing words** |
| **13:00** | **Departure** |

### 2.1.7 Report on Workshop ”Charge Transfer in Biosystems”

**Place: Universitätszentrum Obergurgl, Austria**

**Date: July 17-22, 2011**

**Sponsors:**
**European Science Foundation;**
**Psi-K;**
**Center S3 CNR Institute of Nanoscience (CNR-NANO-S3), Modena, IT;**
**Karlsruhe Institute of Technology (KIT), DE.**

**Organizers:**
**Rosa Di Felice (CNR-NANO-S3, IT);**
**Yuri Berlin (Northwestern University, US);**
**Marcus Elstner (KIT, DE).**

**Web Page:** `http://www.esf.org/activities/esf-conferences/details/2011/confdetail354.html`

#### Report

The issue of charge transfer in biosystems is a hot topic in the scientific community since decades, especially due to its relevance in biology and medicine. The advent of nanotechnology and in particular the use of biomolecules in devices has rekindled the interest in this field. This situation has generated the confluence of many different approaches to study the problem. For instance, traditionally measurements of charge transfer were done on molecular ensembles in solution (chemistry groups), while now one can also measure electrical currents through single molecules between electrodes (physics groups): what is the relation between the transfer rates measured in solution and the electrical currents measured in devices? Theoretical methods are also merging and competing: is it better to compute transfer integrals at a high accuracy level for small frozen fragments or is it better to do simplified semi-empirical simulations of entire fluctuating molecules? What is the role of self-interaction corrections? Is it important to go beyond the two-state approximation? All these problems were debated during the conference. A particularly relevant aspect, that was repeatedly raised during the plenary and informal discussions, is the relation between theory and experiment: how can the theorists communicate easily to the experimentalists what are the shortcomings of the existing theoretical methods for which the interpretation of experiments is not always clear and unanimous? How can experiments be employed to validate theories? Can we plan benchmark experiments that effectively assess theoretical/computational results? Can we identify small benchmark biosystems on which we can appraise different approximations in the existing methods? I remark the lively dialogue between theorists and experimentalists at the conference. The conference was successful from several viewpoints:

- It really brought together different communities with diverse expertise and multi-disciplinary background (physics, biology, chemistry, engineering);
- It created an informal atmosphere that enabled unbiased discussions;
- It effectively brought into play early stage researchers, who animatedly participated not only in the oral/poster program but also in the discussions;
- It created new contacts between scientists, likely promoting future collaborative projects;
- There was a very high scientific quality of the presentations;
- The participants were quite satisfied of all the aspects of the conference, including the science, the organization, the venue, the social program, the professional response of the staff to any sudden request.

Conference summary.

The first introductory session was devised to set the basics of charge transfer theory and its relation to the quantum theory of conductivity. Two invited lectures fulfilled this scope.

Spiros Skourtis emphasized the role of environmental fluctuations and the need for enhanced sampling techniques: not only time enhanced sampling, but general methods to improved tha statistics and account for rare events. He then discussed an application to bacteria nanowires that are essentially 2-dimensional networks of cytochromes with high packing and high order. These systems were also the topic of an experimental talk later in the program and a lively discussion soon arose.

Abraham Nitzan talked about current transfer, explaining the relevance of transfer not only of the position but also of the momentum. He introduced magnetic effects and the excitation of circular currents. He presented studies on simple model systems, namely benzene rings.

The two invited lectures were complemented by 2 short talks on applications of theory and computation. The discussion at the end of the session was characterized by the question: What distinguished electron transfer in biological systems from electron transfer in other systems? It emerged that model systems can be used to study the basics of charge transfer mechanisms, but different systems have peculiarities.

Two sessions (2 and 7) were devoted to computational approaches to charge transfer.

Nicola Marzari (invited) talked about the relevance of the self-interaction correction. He discussed the oxidation of Fe ions in water and short-range self-interaction in transition-metal chemistry, where he showed that GGA+U theory works.

Alessandro Troisi (invited) discussed the relation between charge transfer in biosystems and organic electronics. He insisted again on the importance of dynamical effects. He presented work on the charge separation at organic/inorganic interfaces, relevant for solar-cell applications.

Gianaurelio Cuniberti (invited) talked about Landauers theory on charge transport and applications to: molecules at surfaces, bioelectronics, molecular materials.

Agostino Migliore (invited) presented new theoretical developments to compute thansfer integrals in DFT using non-orthogonal diabatic states.

Ferdinand Grozema (invited) talked about the electronic structure and excited states in DNA hairpins from computational approaches.

Jochen Blumberger (invited) presented large-scale molecular simulations of protein systems.

David Bowler presented linear scaling constrained density functional theory (DFT), with examples of scaling for Si and Ge and application to DNA and proteins. Thorsten Hansens work was based on non-equilibrium Greens functions techniques. Michele Pavanello discussed the relevance of the amount of exact exchange contributions in the DFT computation of transfer integrals with hybrid functionals. Michael Zwolak talked about computational studies of DNA sequencing: he remarked, once again, the paramount importance of structural fluctuations. Tomas Kubar presented a scheme to effectively account for fluctuations in computational investigations, based on SCC-DFTB and QM/MM.

Discussion on theory aspects.
(1) Transfer integrals calculations: need for benchmark systems to validate theories and experimental approaches.
(2) $\lambda$, $\Delta$G: need for polarizable force fields.
(3) Importance of the initial state for the charge-transfer reaction.

Two sessions (3 and 5) were devoted to charge transfer/transport in proteins and complex biological systems.

Leslie Duttons (invited) work is devoted to understanding elementary processes of oxidation-reduction and diverse biological events coupled to it. He explores biological redox reactions and possibility of engineering photochemistry.

Paolo Facci (invited) presented experimental work done on single biomolecules with the electrochemical scanning tunneling microscope.

Krystof Bobrowski (invited) introduced the radiation-induced electron-transfer in enkephalins. He discussed experimental work on two different kinds of enkephalins, with either Leu or Met at the C terminal. Radiation is an alternative method to induce charge transfer, relative to the widely employed photochemistry.

Bernd Giese (invited) gave an overview on the significant experimental contribution of his group to elucidate charge transfer in DNA through the years. Then he focused on new work on peptide assays for electron transfer. He discussed through-bond electron transfer, connection to photosystems, water mediation, the role of charges.

Among the short talks in these sessions, I point out the work of Moh El-Naggar on bacteria nanowires, who carried out transport measurements on lithographic electrodes, revealing high currents probably due to the network of cytochromes. Carlo Bortolotti presented a dynamical view of cytochrome C from electrochemistry measurements. Lior Sepunaru presented current measurements in protein layers between electrodes, revealing fingerprints of unfolding by varying the temperature. The discussion on experiments focused on how to understand the mechanisms of charge transfer through DNA: how does the polaron model match with superexchange? What are good experiments to prove the existence of polarons? Though precise answers did not emerge, these critical issues were identified for future directives.

One session (4) was devoted to DNA conductance and charge transport in DNA molecular junctions. The only invited lectures, Danny Porath, reviewed the pioneering work done by him and his collaborators to enable and understand measurements of electrical currents through single DNA molecules between nanoscale electrodes. He then presented new developments on more complex biosystems.

Two sessions (6 and 8) were devoted to charge migration and excitations in DNA. All the invited lectures presented experimental work and discussed various methods and systems, including photochemistry and electrochemistry, as well as various DNA modifications with metal inclusion and with photoactive elements. It emerged that, despite the long years of investigation, a clear understanding of the charge transfer mechanisms still deserves attention, especially if DNA is to be exploited for nanotechnologies.

### Conference Program

The conference program included 8 oral topical sessions and 1 poster session. The posters stayed on the boards for the duration of the conference. The oral sessions included invited lectures of 40 minutes each and short talks of 20 min each. The latter were selected among the submitted abstract, which were overall of high quality. In the details below, names of invited speakers are in bold characters. Each oral session was concluded with a discussion phase.

The poster session was preceded by a flash presentation of posters, in which the early stage researchers who presented posters could illustrate with one slide the contents of their posters to the audience. There was an excursion that stimulated informal discussions among the participants: it was attended by almost all participants. There was a final Forward Look Plenary Discussion in the evening of the last program day (Thursday July 21), in which we discussed the stat-of-the-art and the challenges for the future, set few goals for the near future and planned a new conference on the same topics, chaired by Rosa Di Felice with co-chairs Bernd Giese and Spiros Skourtis.

Names of invited speakers are in bold in the program table.

| Sunday, July 17 | |
|---|---|
| 18:00 onwards | **Registration at the ESF Desk** |
| 19:00 | **Welcome Drink** |
| 19:30 | **Dinner** |

| Monday, July 18 | |
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| 9:20-9:40 | **Welcome Address** |
| **Session 1: Theory of charge transfer and relation to charge transport**<br>Session Chair: Yuri Berlin | |
| 9:40-10:20 | **Spiros Skourtis**, University of Cyprus, CY.<br>*Modeling electron transfer and transport from the molecular to the cellular length scales* |
| 10:20-10:40 | Emilie Cauët, University Libre de Bruxelles, BE.<br>*Hole-trapping property of the human telomere sequence* |
| 10:40-11:00 | **Coffee Break** |
| 11:00-11:20 | Vladimir Egorov, Russian Academy of Science, RU.<br>*Novel theory of charge transfers in condensed matter and its correlation with experiment: Optical line shapes for polymethine dyes and their aggregates* |
| 11:20-12:00 | **Abraham Nitzan**, Tel Aviv University, IL.<br>*Circular currents, current transfer and magnetic field effects in molecular wires* |
| 12:00-12:40 | **Discussion** |
| 13:00-15:00 | **Lunch Break and Informal Discussion** |
| **Session 2: Computational approaches to charge transfer (I)**<br>Session Chair: Rosa Di Felice | |
| 15:00-15:40 | **Nicola Marzari**, Oxford University, UK.<br>*Charge transfer from first-principles: challenges and solutions* |
| 15:40-16:00 | David Bowler, University College London, UK.<br>*Charge transfer in large systems with linear scaling constrained DFT* |
| 16:00-16:20 | Thorsten Hansen, Lund University, SE.<br>*Non-equilibrium Greens function theory of 2D electronic spectroscopy* |
| 16:20-16:40 | **Coffee Break** |
| 16:40-17:20 | **Alessandro Troisi**, University of Warwick, UK.<br>*What can we learn about charge transfer in biosystems from organic electronics?* |

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|---|---|
| 17:20-17:40 | Michele Pavanello, Leiden University, NL.<br>*Charge transfer in biological systems studied by subsystem density functional theory* |
| 17:40-18:00 | Michael Zwolak, Los Alamos National Laboratory, US.<br>*Rapid DNA sequencing via transverse electronic transport* |
| 18:00-18:20 | Tomas Kubar, Karlsruhe Institute of Technology, DE.<br>*Non-adiabatic simulation of charge transfer in DNA* |
| 18:20-19:00 | **Gianaurelio Cuniberti**, TU Dresden, DE.<br>*From molecular wires to organic semiconductors and back - some dont ask, dont tell of soft electronics* |
| 19:00-19:40 | Discussion |
| 20:00 | **Dinner** |

## Tuesday, July 19

**Session 3: Charge transfer/transport in proteins and complex biological systems (I)**

Session Chair: Danny Porath

| | |
|---|---|
| 9:00-9:40 | **P. Leslie Dutton**, University of Pennsylvania, US.<br>*Molecular engineering of photochemical charge* |
| 9:40-10:00 | Nurit Ashkenasy, Ben Gurion University, IL.<br>*Charge transfer through, and from, artificial proteins in solid state configurations* |
| 10:00-10:20 | Samita Basu, Saha Institute of Nuclear Physics, IN.<br>*Magnetic field effect on photoinduced electron transfer between calf thymus DNA and ternary copper complex* |
| 10:20-10:40 | **Group Photo** |
| 10:40-11:00 | **Coffee Break** |
| 11:00-11:40 | **Paolo Facci**, CNR-NANO-S3 Modena, IT.<br>*ECSTM/STS investigation of single molecules bearing two redox levels* |
| 11:40-12:00 | Eduardo Della Pia, Cardiff University, UK.<br>*Observations of conductance gating for a single-redox engineered protein junction* |
| 12:00-12:20 | Randall Thomas Irvin, University of Alberta, CA.<br>*Spontaneous modulation of the electronic state of stainless steel via a novel synthetic bio-metallic interface* |
| 12:20-12:40 | Liliana Radu, Ministry of Health Romania, RO.<br>*Fluorescence resonance energy transfer in the investigation of normal and tumoral chromatin structure* |

| | |
|---|---|
| 12:40-13:00 | **Discussion** |
| 13:00-15:00 | **Lunch Break and Informal Discussion** |

**Session 4: DNA conductance and charge transport in DNA molecular junctions**

Session Chair: Abraham Nitzan

| | |
|---|---|
| 15:00-15:40 | **Danny Porath**, Hebrew University of Jerusalem, IL.<br>*Charge transport and spectroscopy in DNA molecules* |
| 15:40-16:00 | Daria Brisker-Klaiman, Technion-Israel Inst. of Technol., IL.<br>*Coherent elastic transport contribution to currents through ordered DNA molecular junctions* |
| 16:00-16:20 | **Coffee Break** |
| 16:20-16:40 | Margarita Dimakogianni, University of Athens, GR.<br>*On the conductivity behaviour of the DNA double helix* |
| 16:40-17:00 | Orsolya Ujsghy, Budapest University of Economics and Technology, HU.<br>*Conductance of DNA molecules: Effects of decoherence and bonding* |
| 17:00-17:20 | Erika Penzo, Columbia University, US.<br>*Directed biomolecular assembly of integrated single molecule devices: toward reliable transport measurements* |
| 17:20-18:30 | **Flash Presentations of Posters** - poster presenters will introduce themselves to the audience and illustrate in one slide the contents and message of their poster |
| 18:30-20:00 | **Poster Session** - posters can remain on the boards for the duration of the conference |
| 20:00 | **Dinner** |
| 21:30-23:00 | **Roundtable Discussion** |

## Wednesday, July 20

**Session 3: Charge transfer/transport in proteins and complex biological systems (II)**

Session Chair: Paolo Facci

| | |
|---|---|
| 9:00-9:40 | **Krzysztof Bobrowski**, Institute of Nuclear Chemistry and Technology, PL.<br>*Radiation-induced electron transfer in enkephalins* |
| 9:40-10:00 | Carlo Augusto Bortolotti, University of Modena, IT.<br>*Transient open of solvent-accessible cavities in Yeast cytochrome c as a tool for fine-tuning of its redox potential* |
| 10:00-10:20 | Lior Sepunaru, Weizmann Institute Rehovot, IL.<br>*Temperature dependent electron transport in proteins* |

| | |
|---|---|
| 10:20-10:40 | Moh El-Naggar, USC Los Angeles, US.<br>*Electron Transfer across the Biotic-Abiotic Interface in Microbial Fuel Cells* |
| 10:40-11:00 | **Coffee Break** |
| 11:00-11:40 | **Bernd Giese**, University of Fribourg, CH.<br>*Electron hopping through peptides: The role of side chains and the backbone* |
| 11:40-12:00 | Stefano Corni, CNR-NANO-S3 Modena, IT.<br>*Electron transfer proteins on gold surfaces investigated by molecular dynamics simulations* |
| 12:00-12:20 | Gilbert Nöll, University of Siegen, DE.<br>*Electrochemical switching of the flavoprotein dodecin on DNA-monolayers* |
| 12:20-12:40 | Brotati Chakraborty, Saha Institute of Nuclear Physics, IN.<br>*Magnetic field effect corroborated with docking study to explore photoinduced electron transfer in drug-protein interaction* |
| 12:40-13:00 | Discussion |
| 13:00-17:30 | **Excursion with lunch box**<br>(lunch will be served as normal for those who will not participate in the excursion) |
| **Session 6: Charge migration and excitations in DNA (I)**<br>Session Chair: Dimitra Markovitsi | |
| 17:40-18:20 | **Gary Schuster**, Georgia Institute of Technology, US.<br>*Radical cation hopping and reaction in DNA* |
| 18:20-18:40 | Irena Kratochvílová, Academy of Sciences of the Czech Republic, CZ.<br>*Charge transport in DNA oligonucleotides with various base-pairing patterns* |
| 18:40-19:00 | John M. Kelly, Trinity College Dublin, IE.<br>*Dipyridophenazine metal complexes which undergo photo-induced electron transfer with DNA* |
| 19:00-19:40 | **Torsten Fiebig**, Northwestern University, US.<br>*Electronic Transfer Processes in Biological and Biomimetic Donor-Acceptor Systems* |
| 19:40-20:00 | Discussion |
| 20:00 | **Drinks Reception and Conference Dinner** |

## Thursday, July 21

### Session 7: Computational approacher to charge transfer (II)

Session Chair: Marcus Elstner

| | |
|---|---|
| 9:00-9:40 | **Agostino Migliore**, Tel Aviv University, IL.<br>*Effective electronic coupling calculation using non orthogonal diabatic states: application to charge transfer in $\pi$-stacks relevant to biochemistry and nano-electronics* |
| 9:40-10:00 | Andrea Ferretti, CNR-NANO-S3, IT.<br>*Hybrid functional and GW corrections to quantum transport calculations* |
| 10:00-10:40 | **Ferdinand Grozema**, Delft University, NL.<br>*Charges and excited states in DNA hairpins: a theoretical study* |
| 10:40-11:00 | **Coffee Break** |
| 11:00-11:40 | **Jochen Blumberger**, University of Cambridge, UK.<br>*Electron transfer in cytochromes, oxidase and bacterial 'wire'-proteins: Insights from molecular computations* |
| 11:40-12:00 | George Kalosakas, University of Patras, GR.<br>*Electronic parameters for charge transfer along DNA* |
| 12:00-12:40 | Discussion |
| 13:00-15:00 | **Lunch Break and Informal Discussion** |

### Session 8: Charge migration and excitations in DNA (II)

Session Chair: Gary Schuster

| | |
|---|---|
| 15:00-15:40 | **Thomas Carell**, Ludwig-Maximilians University, DE.<br>*Metal-base pairs and metal containing DNA* |
| 15:40-16:20 | **Dimitra Markovitsi**, CEA Saclay, FR.<br>*Electronic excited states and reactivity of DNA* |
| 16:20-16:40 | **Coffee Break** |
| 16:40-17:00 | Frank Garwe, IPHT Jena, DE.<br>*Long-range energy transfer in DNA after fs laser pulse excitation of silver nanoparticle neighboured to DNA* |
| 17:00-17:20 | Rudy Schlaf, University of South Florida, US.<br>*Electronic structure of self-assembled peptide nucleic acid thin films* |
| 17:20-18:00 | **Jason Slinker**, University of Texas at Dallas, US.<br>*Fundamentals of DNA-mediated electrochemistry* |
| 18:00-18:20 | Marcos Brown Goncalves, University of Sao Paulo, BR.<br>*Theoretical study of metal DNA structures* |
| 18:20-19:00 | **Hans-Achim Wagenknecht**, University of Regensburg, DE.<br>*Photoinduced electron transfer in synthetically modified DNA* |
| 19:00-19:40 | Discussion and Summary |

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|---|---|
| 20:00 | **Dinner** |
| 21:30-23:00 | **Forward Look Plenary Discussion**<br>Coordinated by Bernd Giese |

| **Friday, July 22** |
|---|
| Breakfast and Departures |

## List of Participants

Invited Speakers and Chairs

1 Berlin Yuri (Chair)

2 Blumberger Jochen

3 Bobrowski Krzysztof

4 Carell Thomas

5 Cuniberti Giovanni

6 Di Felice Rosa (Chair)

7 Dutton P. Leslie

8 Elstner Marcus (Chair)

9 Facci Paolo

10 Fiebig Torsten

11 Giese Bernd

12 Grozema Ferdinand

13 Markovitsi Dimitra

14 Marzari Nicola

15 Migliore Agostino

16 Nitzan Abraham

17 Porath Danny

18 Schuster Gary

19 Skourtis Spiros

20 Slinker Jason

21 Troisi Alessandro

22 Wagenknecht Hans-Achim

Accepted Applicants

1 Ak Jissy

2 Amdursky Nadav

3 Artes Vivancos Juan Manuel

4 Ashkenasy Nurit

5 Banerjee Mousumi

6 Basu Samita

7 Bende Attila

8 Berstis Laura

9 Borges Anders

10 Bortolotti Carlo Augusto

11 Bowler David

12 Brazdova Veronika

13 Breuer Marian

14 Brisker-Klaiman Daria

15 Camargo Dalmatti Alves Lima Filipe

16 Cauët Emilie

17 Caycedo-Soler Felipe

18 Chakraborty Brotati

19 Corni Stefano

20 Davis Elisabeth

21 Della Pia Eduardo Antonio

22 Di Paolo Gaia

23 Dimakogianni Margarita

24 Dorner Ross

25 Egorov Vladimir V.

26 El-Naggar Moh

27 Èoga Lucija

28 Ferreiro Dardo Nahuel

29 Garwe Frank

30 Goncalves Marcos

31 Hansen Thorsten

32 Irvin Randall Thomas

33 Kalosakas George

34 Kelly John

35 Kim Heeyoung

36 Kratochvilova Irena

37 Kubar Tomas

38 Macdonald John Emyr

39 Nöll Gilbert

40 Omerzu Ales

41 Ouahab Lahcène

42 Pavanello Michele

43 Penzo Erika

44 Plasser Felix

45 Quinn Susan

46 Radu Liliana

47 Sarangi Manas

48 Schlaf Rudy

49 Sepunaru Lior

50 Solomon Gemma

51 Torrellas Germán

52 Ujsághy Orsolya

53 Varsano Daniele

54 Woiczikowski Benjamin

55 Wolter Mario

56 Zakrassov Alexander

57 Zilly Matias

58 Zwolak Michael

59 Ferretti Andrea

### 2.1.8 Report on Hands-On Tutorial: Density Functional Theory and Beyond, Concepts and Applications

**Berlin, July 12 - 21, 2011**

**Sponsors: Max Planck Society, CECAM, ESF, Psi-k, DFG, NEC**

**Organizers: Volker Blum, Heiko Appel, Matthias Scheffler**

**Web page:** `http://www.fhi-berlin.mpg.de/th/Meetings/DFT-workshop-Berlin2011/`

#### Summary

We have organized and implemented a successful ten-day workshop on the concepts and applications behind modern electronic structure theory ("density functional theory and beyond") for computational materials science, held from July 12-21, 2011 at the Harnackhaus conference center and Fritz Haber Institute in Berlin, Germany. The workshop brought together an audience of more than 80 students and post-docs (108 including tutors from the Fritz Haber Institute) for 23 keynote lectures on the basics and selected advanced topics from the field, as well as six afternoon "hands-on" tutorials with computers and one weekend "hands-on" tutorial and research project. In addition, a "poster parade" on the first day and poster session on the second day provided each participant with an opportunity to introduce themselves and their work to the entire group, a key step to foster communication, information exchange, and ultimately, trust between the initially unconnected set of participants. Computer-based electronic structure theory from quantum-mechanical first principles is a rapidly growing field with a multitude of practical applications in condensed matter physics, materials science, nanoscience, (bio)molecular science, pharmacology, and other disciplines. The versatility of the field can also create a significant entry barrier especially for newly incoming researchers. The goal of the work was to provide such an entry into the field (by the more basic keynote lectures) and widening of scope (by the more advanced keynote lectures) for its entire audience.

Out of the more than 160 applicants, we were able to accommodate 80 external participants who formed a highly motivated, active audience not only in the tutorials, but also during the entire set of keynote lectures offered at the workshop. As in a previous event, we found the Harnackhaus conference center an excellent venue for the event, allowing to use the infrastructure of the nearby (50 metres) Fritz Haber Institute for the computational exercises rather efficiently. Aside from the actively tutored sessions, the computer facilities were available to all participants throughout the workshop, both for additional late-evening sessions with tutors on hand and for independent work. The showing even outside the regular afternoon and evening sessions amounted to a significant fraction of the participants—for example, we estimate that more than 50 % of the participants made regular use of the additional evening sessions. We also note that the workshop could not have been successful without the large efforts of the tutors at the Fritz Haber Institute (and, in two cases, externally at Brigham Young University in Provo, Utah—Prof. Gus Hart and Lance Nelson) to create and perfect the specific, guided tutorials at the workshop.

### Description of the scientific content of and discussion at the event

Topically, the workshop was (roughly) split into three parts: a set of broader topics covering the scientific basics of the field (July 12-15), a weekend tutorial and research project (July 16 and 17), and a set of focused, advanced topics towards the frontiers of the field (July 18-21). Two overview lectures on July 12 covered the broader topics of electronic structure theory (Scheffler) and quantum chemistry (Sauer), followed by a "poster parade" that allowed each participant to introduce themselves and their research interest. The practical basics of density functional theory occupied the two first full days (July 13/14; Della Sala, Blum, Wieferink, Levchenko, Ambrosch-Draxl, Marsman), covering practical exchange-correlation approximations, and implementation aspects across three major code frameworks, including details of periodic systems, and capped by two introductory tutorials on these topics. July 15 covered some more advanced methodological foundations (time-dependent density functional theory, van der Waals interactions, and many-body perturbation approaches; Gross, Tkatchenko, Ren), flanked by a tutorial introducing the "weekend research project" (July 16/17): Structure prediction of biologically relevant molecules (two amino-acid peptides) and the role of different exchange-correlation aspects in these systems. The second week was split as follows: Ground state and multiscale-type approaches (Ghiringhelli, Hart, Walsh; July 18), *ab initio* molecular dynamics and time-dependent phenomena (Car, Carbogno, Appel; July 19), electronic phenomena beyond ground-state approaches (Rinke, Biermann, Guo; July 20), and finally, some of the methodological frontiers of the field in real-world modelling settings (Reuter, Lampenscherf, Schulthess; July 21). July 18-20 saw corresponding tutorials that were directly integrated with the morning sessions and co-prepared by some of the speakers.

Based on the response of the participants, both to the actual keynote lectures (questions and discussions) and during the tutorials, we feel that we were able to maintain a high level of impact throughout the workshop. We believe that this success was helped by the mix of keynote speakers present, both local experts from FHI and high-profile, leading experts in the field (Sauer, Della Sala, Ambrosch-Draxl, Marsman, Gross, Hart, Walsh, Car, Biermann, Guo, Reuter, Schulthess). Likewise, the enormous efforts of the local tutorial organizers and tutors were essential to the success of the event. Without these elaborate preparations and active support by a large group of individuals (approx. 25) at FHI and elsewhere, the event could not have been successful.

### Assessment of the results and impact of the event on the future direction of the field

The field of electronic structure theory is rather large today. Yet, aside from a small set of common basics, much of the field is not part of university curricula even at the graduate level in our experience. Based on the response from the participants, we believe that our attempt to link an in-depth introduction to the methodological basics with an ambitious range of advanced topics at the forefront of the field was a success. The impact of this event can perhaps be gauged in relation to past events — the workshop format in question happens since 1994 in intervals of roughly every two years, at FHI. The fact that 160 participants applied despite strong competition from parallel, unrelated workshops at a European scale within the same time frame shows, in our opinion, the need for comprehensive events such as ours more than anything else.

Apart from the discussions and tutorials held at the workshop, the results are available permanently on the world-wide web at:

`http://www.fhi-berlin.mpg.de/th/Meetings/DFT-workshop-Berlin2011/`

including links to all presentation slides and tutorial materials used at the workshop. We hope to have brought together, through our workshop, a diverse group of motivated researchers that are now coming into the field. In our experience, some of the ties formed at such events can last across significant parts of scientific careers, and instill long-term ideas in minds that are still fresh and unbiased enough to see them through. The goal of this workshop was to provide support to future researchers willing to make an impact in the field, and we hope that this first step was a success.

### Program of the Hands-On 2011 Tutorial

| **Tuesday, July 12:** | **The Big Picture: Electronic Structure Theory** |
|---|---|
| 11:30-14:30 | Registration |
| 14:30-14:45 | Introductory remarks |
| 14:45-15:45 | Matthias Scheffler (FHI Berlin) - Computational materials sciences from first principles: Status, achievements, challenges |
| 15:45-16:45 | Joachim Sauer (HU Berlin) - Quantum Chemistry and wave function based methods |
| 16:45-17:15 | Break |
| 17:15-20:00 | Poster parade (2 min. talks by all participants) |
| 20:00-22:00 | Welcome Dinner |

| **Wednesday, July 13:** | **The Basics of Density Functional Theory** |
|---|---|
| 6:30-9:00 | Breakfast |
| 9:00-10:00 | Fabio Della Sala (NNL, Lecce) - XC functionals for the ground state |
| 10:00-11:00 | Volker Blum (FHI Berlin) - The nuts and bolts of electronic structure theory: basis sets, grids, relativity etc. |
| 11:00-11:30 | Break |
| 11:30-12:30 | Jürgen Wieferink (FHI Berlin) - The nuts and bolts of electronic structure theory (II): Self-consistency, gradients, relaxation and vibrations |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 1 - The basics of electronic structure theory (V. Atalla, O. Hofmann, S. Levchenko), presentation, instructions |
| 18:30-20:00 | Dinner |
| 20:00-22:00 | Poster session for participants (posters will be up for the whole week) |

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|---|---|
| **Thursday, July 14:** | **Periodic Systems** |
| 6:30-9:00 | Breakfast |
| 9:00-10:00 | Sergey Levchenko (FHI Berlin) - Basics for periodic systems |
| 10:00-11:00 | Claudia Ambrosch-Draxl (Uni Leoben) - LAPW and related methods: the example of the Exciting code |
| 11:00-11:30 | Break |
| 11:30-12:30 | Martijn Marsman (Uni Wien) - Plane wave methods, pseudopotentials, and PAW: the example of the VASP code |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 2 - Periodic systems: Solids, surfaces, band structure and reconstruction (J. Wieferink, L. Nemec), presentation, instructions |
| 18:30-20:00 | Dinner |
| 20:00-22:00 | Extra computer time with tutors on hand |

| | |
|---|---|
| **Friday, July 15:** | **Beyond LDA/GGA** |
| 6:30-9:00 | Breakfast |
| 9:00-10:00 | Hardy Gross (MPI Halle) - XC beyond static DFT |
| 10:00-11:00 | Alexandre Tkatchenko (FHI Berlin) - Approaches to van der Waals |
| 11:00-11:30 | Break |
| 11:30-12:30 | Xinguo Ren (FHI Berlin) - Beyond LDA and GGA in practice |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 3 - Weekend research project (beginning): Conformational space and energetics of (bio)molecules: Physical concepts and performance of DFT-based and correlated methods<br>(A. Tkatchenko, C. Baldauf, M. Ropo), presentation, instructions |
| 18:30-20:00 | Dinner |
| 20:00-22:00 | Extra computer time with tutors on hand |

| | |
|---|---|
| **Saturday, July 16** | |
| 6:30-9:30 | Breakfast |
| 9:00-13:00 | Weekend research project with tutors on hand |
| 14:00- | Berlin Excursion (open end, see separate schedule) |

| | |
|---|---|
| **Sunday, July 17** | |
| 7:00-10:00 | Breakfast |
| all day | Weekend research project with tutors on hand<br>(incl. light ”working lunch” at the lecture hall) |
| 18:30-20:00 | ”Working Dinner” |

| | |
|---|---|
| **Monday, July 18:** | **Ab initio Thermodynamics** |
| 6:30-9:00 | Breakfast |

| | |
|---|---|
| 9:00-10:00 | Elizabeth C. Beret / Luca Ghiringhelli (FHI Berlin) - Ab initio atomistic thermodynamics |
| 10:00-11:00 | Gus Hart (Brigham Young University) - Cluster expansion and multiscale modelling |
| 11:00-11:30 | Break |
| 11:30-12:30 | Aron Walsh (UCL London) - Modelling materials and processes for solar cells |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 4 - Multiscale modeling of configurational energetics (G. Hart, V. Blum, N. Richter), presentation, instructions |
| 18:30-20:00 | Dinner |
| 20:00-20:30 | Matthias Scheffler (FHI) - One hundred years of science in Dahlem: History of the FHI and of the MPG |
| 20:30-22:00 | Extra computer time with tutors on hand |

| **Tuesday, July 19:** | **Molecular Dynamics and Time-Dependent DFT** |
|---|---|
| 9:00-10:00 | Roberto Car (Princeton) - Ab initio molecular dynamics: from the basics up to quantum effects |
| 10:00-11:00 | Christian Carbogno (FHI Berlin and UC Santa Barbara) - Thermostats and thermal transport in solids |
| 11:00-11:30 | Break |
| 11:30-12:30 | Heiko Appel (FHI Berlin) - Introduction to real-space, linear-response, and time-dependent methods: the example of the Octopus code |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 5 - Phonons, molecular dynamics and free energies for solids (C. Carbogno, L. Ghiringhelli, M. Rossi), presentation part 1, presentation part 2, instructions |
| 18:30-20:00 | Dinner |
| 20:00-22:00 | Extra computer time with tutors on hand |

| **Wednesday, July 20:** | **Spectroscopy and Transport** |
|---|---|
| 6:30-9:00 | Breakfast |
| 9:00-10:00 | Patrick Rinke (FHI Berlin) - Excited states and GW/BSE |
| 10:00-11:00 | Silke Biermann (Ecole Polytechnique, Palaiseau) - Strong correlation - what is it, and how to tackle it (DMFT) |
| 11:00-11:30 | Break |
| 11:30-12:30 | Hong Guo (McGill University) - Basics of electronic transport |
| 12:30-14:00 | Lunch |
| 14:00-18:00 | Practical session 6 - Computational spectroscopy (H. Appel, P. Rinke, F. Caruso), presentation, instructions |
| 18:30-20:00 | Dinner |
| 20:00-22:00 | Extra computer time with tutors on hand |

| **Thursday, July 21:** | **Electronic Structure Frontiers** |
|---|---|
| 6:30-9:00 | Breakfast |
| 09:00-10:00 | Karsten Reuter (TU München) - Towards first-principles chemical engineering |
| 10:00-11:00 | Stefan Lampenscherf (Siemens AG, Corporate Technology) - Electronic structure theory in industry |
| 11:00-11:30 | Break |
| 11:30-12:30 | Thomas Schulthess (ETH Zürich) - Electronic structure theory at the petascale and beyond |
| 12:30-14:00 | Lunch and End of Workshop |

## 2.2 Psi-k Workshop Announcements

### 2.2.1 Workshop on Ab initio Description of Iron and Steel (ADIS2012): Thermodynamics and Kinetics

**Ringberg Castle (Tegernsee, Germany)**

**April 29 to May 04, 2012**

**MPIE, ICAMS, SFB761**

**T. Hickel, C. Race, R. Drautz, J. Neugebauer**

`http://ADIS2012.mpie.de`

We would like to draw your attention to our fourth international workshop in the series “Ab initio Description of Iron and Steel (ADIS2012)”. This year the workshop will take place in spring at Ringberg Castle, which is beautifully located in the foothills of the Bavarian Alps (Germany) overlooking lake Tegernsee.

During the workshop various ab initio approaches and thermodynamic as well as kinetic methods to model finite-temperature properties, processes and phase transitions will be discussed. In addition the comparison with more empirical approaches, such as Calphad and Dictra, will be an important topic of the workshop. Key experts in these fields agreed to give tutorial-like lectures on recent methodological advances and successful applications. The confirmed invited speakers are:

- Igor Abrikosov (Linkping University, Sweden)
- Dario Alfé (University College London, UK)
- Sergei L. Dudarev (UKAEA Culham, UK)
- Peter Entel (University of Duisburg-Essen, Germany)
- Subhradip Ghosh (IIT Guwahati, India)
- Blazej Grabowski (Lawrence Livermore National Lab, USA)
- Bengt Hallstedt (RWTH Aachen University, Germany)
- Zi-Kui Liu (Penn State University, USA)
- Daniel Mason (Imperial College London, UK)
- Stefan Müller (TU Hamburg - Harburg, Germany)
- Andrei Ruban (KTH Stockholm, Sweden)
- Marcel Sluiter (TU Delft, The Netherlands)

- Frédéric Soisson (CEA Saclay, France)
- George Smith (University of Oxford, UK)
- George Malcolm Stocks (Oak Ridge National Lab, USA)
- Adrian Sutton (Imperial College London, UK)

Extensive inroductions to the different methods will enable young researchers to contribute actively to the discussions. All participants will have the opportunity to present their results in poster sessions. A small number of 30-minute oral contributions will also be possible.

The workshop is organized by the Max-Planck-Institut für Eisenforschung in Düsseldorf (T. Hickel, C. Race and J. Neugebauer, Department of Computational Materials Design) together with a colleague from the Interdisciplinary Centre for Advanced Materials Simulations in Bochum (R. Drautz, Department for Atomistic Modelling and Simulation). It is part of the activities of the collaborative research centre "Steel ab initio" (SFB761, http://stahl-abinitio.de), which provides most of the financial support. The research centre is devoted to quantum-mechanically guided design of new Fe-based materials, with a particular focus on high-Mn steels.

The fee for regular participants (covering accommodation and all meals) is 650 EUR, students may apply for a reduced fee (500 EUR). The number of participants is limited to 60. If you are interested, we therefore advise you to send an application as soon as possible to adis2012@mpie.de. The application/abstract submission deadline is March 1, 2012.

We look forward to meeting you at Ringberg castle,

Tilmann Hickel
Chris Race
Ralf Drautz
Jörg Neugebauer

### 2.2.2 Summer School on "Bandstructure meets many body theory"

**Vienna**

**September 18-22, 2012**

**Sponsors: $\Psi_k$, CECAM, SFB ViCom**

**Organizers: K. Held, G. Kresse (Vienna)**

A particular challenge of computational materials science is the calculation of materials in the presence of strong electronic correlations and exchange. In this case, the local density approximation (LDA) or generalized gradient approximation to the exchange correlation potential often yield unreliable results. In recent years we have seen tremendous progress in this field. The aim of the Summer School is to educate the next generation of scientists in both, bandstructure and many body theory. To this end, we will have lectures in the morning and hands-on tutorials in the afternoon by the following speakers on the following topics.

**Invited speakers**

- C. Ambrosch-Draxl (Berlin, LDA)
- S. Biermann (Paris, GW+DMFT)
- P. Blaha (Vienna LDA, LDA+U tutorial)
- R. Godby (York, GW)
- E.K.U. Gross (MPI Halle, TDDFT)
- M. P. Head-Gordon (Berkeley, quantum chemistry)
- J. Kunes (Prague, Wannier functions tutorial)
- R. Noack (Marburg, DMRG)
- G. Sangiovanni (Würzburg, DMFT tutorial)
- A. Toschi (Vienna, quantum field theory)
- M. Towler (Cambridge, QMC)
- R.T. Scalettar (Davis, lattice QMC tutorial)
- D. Vollhardt (Augsburg, DMFT)

How-to-apply: visit our webpage http://www.sfb-vicom.at/summer-schools

Deadline for applications: 31. May 2012

## 2.3 Reports on Collaborative Visits funded by Psi-k

### 2.3.1 Report on a Collaborative Visit of A Marini (Rome) to NEEL Institute (Grenoble)

### Final Report on a Short Visit Grant on ”Non-equilibrium dynamics from first principles”

**A. Marini**
**Physics Department, University of Rome ’Tor Vergata’**
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**www.yambo-code.org/andrea**

**Purpose of the visit**

The purpose of the visit in the group Theory and Numerical Simulation of Electronic Properties at the NEEL laboratory (neel.cnrs.fr), was to develop theoretical approaches, algorithms and numerical codes to simulate the physical properties of realistic systems out-of-the-equilibrium.

In addition to the tight collaboration with the theoretical group of Prof. BLASE the visit was supposed to promote discussions with local members of the institute that are currently involved in the study of models and theoretical approaches to the study of transport in nano-scale materials.

**Description of the work carried out during the visit**

Much to my satisfation, during my visit, I had the opportunity to have deep and exhaustive discussions with two members of the NEEL laboratory: Dr. Simone FRATINI and Dr. Didier MAYOU on the theoretical approaches to the study of non-equilibrium transport they have derived. I also had the opportunity to discuss with Dr. Yann-Michel NIQUET, of the local Atomistic simulation laboratory, about the numerical and theoretical tools he uses to describe intrinsic transport properties in nano-scale materials.

At the same time I continued my fruitful collaboration with Dr. Claudio ATTACCALITE of the NEEL institute on the device of a controllable approach to the non-equilibrium dynamics in realistic materials. With Dr. ATTACCALITE I discussed further projects to be carried on in the following months and we had also very constructive discussions on various theoretical aspects of the non-equilibrium dynamics.

**Description of the main results obtained**

The discussions with the members of the local scientific community gave me an extended overview of the state-of-the-art approaches to the non-equilibrium dynamics, as far as transport properties are concerned. I received several references to review papers and works carried on in the NEEL institute. These will represent a basis for my future work and for future collaborations.

With Dr. ATTACCALITE I discussed the steps necessary to embody the electron-phonon scattering in the non-equilibrium dynamics. We derived a coherent approach to describe the temperature evolution as due to the relaxation of the electronic degrees of freedom following the excitation by means of an ultra-strong laser pulse.

We also discussed further applications of the approach we proposed [1] recently such as: second and third harmonic generation in carbon nano-tubes and the description of the dynamical Franz-Keldysh effect from first principles.

### Future collaboration with host institution

The collaboration with Dr. ATTACCALITE will continue in the forthcoming months. We are already collaborating and, thanks to this visit, new projects have been planned for the future. I will also start a project on conductivity and mobility in molecular crystals. This will permit me to start collaborations with other members of the NEEL institute.

### Projected publications/articles resulting or to result from your grant

There are several publications that will result from the present grant. The study of second and third harmonics generation in carbon nano-tubes, the modeling of electron-phonon scattering (with Dr. ATTACCALITE) and my separate project on conductivity and mobility in molecular crystals. These projects are expected to be concluded by the summer of 2012.

References

[1]. Real-time approach to the optical properties of solids and nanostructures: Time-dependent Bethe-Salpeter equation, by C. Attaccalite, M. Gruning and A. Marini, Phys. Rev. B, in press.

# 3 General Job Announcements

## Postdoctoral and Ph. D Position at Vienna University of Technology, Austria

We announce the opening for a postdoctoral and a Ph.D. position in theoretical solid state physics at Vienna University of Technology with a focus on strongly correlated electron systems and/or computational materials science. The Ph.D. candidate should be truly talented in theoretical and/or computational physics and highly motivated. The postdoctoral candidate should also have working experience in one of the following research areas:

- density functional theory/local density approximation (LDA)
- dynamical mean field theory (DMFT) and extensions (diagrammatic, cluster)
- quantum field theory

Research topics can be either method development or physical understanding (modelling and ab initio calculations) in the general directions of

- interfacing LDA/GW with DMFT
- dynamical vertex approximation
- quantum criticality
- superconductivity
- f-electron systems

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More information concerning the group is available at http://www.ifp.tuwien.ac.at/cms.

Please send applications to Prof. Karsten Held (held@ifp.tuwien.ac.at).

# 4 Abstracts

## Linear-scaling DFT+U with full local orbital optimization

David D. O'Regan[1,2], Nicholas D. M. Hine[1,3], Mike C. Payne[1], and Arash A. Mostofi[3]
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### Abstract

We present an approach to the DFT+$U$ method (Density Functional Theory + Hubbard model) within which the computational effort for calculation of ground state energies and forces scales linearly with system size. We employ a formulation of the Hubbard model using nonorthogonal projector functions to define the localized subspaces, and apply it to a local-orbital DFT method including *in situ* orbital optimization. The resulting approach thus combines linear-scaling and systematic variational convergence. We demonstrate the scaling of the method by applying it to nickel oxide nano-clusters exceeding $7,000$ atoms.

(Submitted to Phys. Rev. B (2011), arXiv:1111.5943)
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# Stacking-Fault Energy and Anti-Invar Effect in FeMn Alloys

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## Abstract

Based on state-of-the-art density-functional-theory methods we calculate the stacking-fault energy of the paramagnetic random Fe-22.5at.%Mn alloy between 300–800 K. We estimate magnetic thermal excitations by considering longitudinal spin-fluctuations. Our results demonstrate that the interplay between the magnetic excitations and the thermal lattice expansion is the main factor determining the anti-Invar effect, the hcp–fcc transformation temperature, and the stacking-fault energy, which is in excellent agreement with measurements.

(Submitted to Phys. Rev. Lett. (2011); available at arXiv.org)

Contact person: Andrei Reyes-Huamantinco (a.huamantinco@mcl.at)

# Unified description of ground and excited states of finite systems: the self-consistent GW approach

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## Abstract

Fully self-consistent *GW* calculations – based on the iterative solution of the Dyson equation – provide an approach for consistently describing ground and excited states on the same quantum mechanical level. We show that for the systems considered here self-consistent *GW* reaches the same final Green function regardless of the initial reference state. Self-consistency systematically improves ionization energies and total energies of closed shell systems compared to $G_0W_0$ based on Hartree-Fock and (semi)local density-functional theory. These improvements also translate to the electron density as exemplified by an improved description of dipole moments and permit us to assess the quality of ground state properties such as bond lengths and vibrational frequencies.

(submitted to Phys. Rev. Lett. (2012))
Contact person: Fabio Caruso (caruso@fhi-berlin.mpg.de)

# Benzene adsorbed on Si(001): The role of electron correlation and finite temperature

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### Abstract

van der Waals energy-corrected density functional theory (DFT + vdW) as well as the exact exchange with electron correlation in the random-phase approximation are used to study the adsorption of benzene on the Si(001) surface with respect to two controversial adsorption structures (termed "butterfly" and "tight bridge"). Our finding that the tight-bridge structure is energetically favored over the butterfly structure agrees with standard DFT but conicts with previous vdW-inclusive calculations. However, the inclusion of zero-point energy and thermal vibrations reverses the stability of the two structures with increasing temperature. Our results provide an explanation for the recent experimental observation that both structures coexist at room temperature.

(Phys. Rev. B **85**, 041403(R) (2012))
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# Resolution-of-identity approach to Hartree-Fock, hybrid density functionals, RPA, MP2, and *GW* with numeric atom-centered orbital basis functions

Xinguo Ren[1], Patrick Rinke[1], Volker Blum[1],
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**Abstract**

We present a computational framework that allows for all-electron Hartree-Fock (HF), hybrid density functionals, random-phase approximation (RPA), second-order Møller-Plesset perturbation theory (MP2), and *GW* calculations based on efficient and accurate numeric atomic-centered orbital (NAO) basis sets. The common feature in these approaches is that their key quantities are expressible in terms of products of single-particle basis functions, which can in turn be expanded in a set of auxiliary basis functions. This is a technique known as the ”resolution of identity (RI)” which facilitates an efficient treatment of both the two-electron Coulomb repulsion integrals (required in all these approaches) as well as the linear response function (required for RPA and *GW*). We propose a simple prescription for constructing the auxiliary basis which can be applied regardless of whether the underlying radial functions have a specific analytical shape (e.g., Gaussian) or are numerically tabulated. We demonstrate the accuracy of our RI implementation for Gaussian and NAO basis functions. Benchmark data that are presented include ionization energies of 50 selected atoms and molecules from the G2 ion test set computed with *GW* and MP2 self-energy approaches, and the G2-I atomization energies and S22 molecular interaction energies with the RPA approach.

(Submitted to New J. Phys. (2012))

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# First-principles optical spectra for $F$ centers in MgO

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## Abstract

The study of the oxygen vacancy ($F$ center) in MgO has been aggravated by the fact that the positively charged and the neutral vacancy ($F^+$ and $F^0$, respectively) absorb at practically identical energies. Here we apply many-body perturbation theory (MBPT) in the $G_0W_0$ approximation and the Bethe-Salpeter approach to calculate the optical absorption and emission spectrum of the oxygen vacancy in all three charge states. We observe unprecedented agreement between the calculated and the experimental optical absorption spectra for the $F^0$ and $F^+$ center. Our calculations reveal that not only the absorption but also the emission spectra of different charge states peak at nearly the same energy, which leads to a reinterpretation of the $F$ center's optical properties.

(In print Phys. Rev. Lett. (2012))

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# Simulation of spin-polarized scanning tunneling microscopy on complex magnetic surfaces: Case of a Cr monolayer on Ag(111)

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### Abstract

We propose an atom-superposition-based method for simulating spin-polarized scanning tunneling microscopy (SP-STM) from first principles. Our approach provides bias dependent STM images in high spatial resolution, with the capability of using either constant current or constant height modes of STM. In addition, topographic and magnetic contributions can clearly be distinguished, which are directly comparable to results of SP-STM experiments in the differential magnetic mode. Advantages of the proposed method are that it is computationally cheap, it is easy to parallelize, and it can employ the results of any ab initio electronic structure code. Its capabilities are illustrated for the prototype frustrated hexagonal antiferromagnetic system, Cr monolayer on Ag(111) in a noncollinear magnetic 120 degrees Néel state. We show evidence that the magnetic contrast is sensitive to the tip electronic structure, and this contrast can be reversed depending on the bias voltage.

(Physical Review B 84, 174428 (2011))
Contact person: Krisztián Palotás, palotas@phy.bme.hu

# Theoretical study of the role of the tip in enhancing the sensitivity of differential conductance tunneling spectroscopy on magnetic surfaces

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**Abstract**

Based on a simple model for spin-polarized scanning tunneling spectroscopy (SP-STS) we study how tip magnetization and electronic structure affects the differential conductance (dI/dV) tunneling spectrum of an Fe(001) surface. We take into account energy dependence of the vacuum decay of electron states, and tip electronic structure either using an ideal model or based on ab initio electronic structure calculation. In the STS approach, topographic and magnetic contributions to dI/dV can clearly be distinguished and analyzed separately. Our results suggest that the sensitivity of STS on a magnetic sample can be tuned and even enhanced by choosing the appropriate magnetic tip and bias set point, and the effect is governed by the effective spin-polarization.

(Physical Review B 83, 214410 (2011))

Contact person: Krisztián Palotás, palotas@phy.bme.hu

# 5 SCIENTIFIC HIGHLIGHT OF THE MONTH

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## Self-Interaction Correction in Density Functional Theory: The Road Less Traveled

Mark R. Pederson[1] and John P. Perdew[2]

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> Two roads diverged in a yellow wood,
> And sorry I could not travel both
> And be one traveler, long I stood
> And looked down one as far as I could
> To where it bent in the undergrowth . . .
> Robert Frost, *The Road Not Taken*, 1920

**Abstract**

The $30^{th}$ anniversary of the Perdew-Zunger paper on the self-interaction correction (SIC) of density functional approximations to the exchange-correlation energy was marked by a recent conference that focused on the theoretical and computational formalism and on diverse applications to insulators, strongly-correlated materials, charge transfer, transport, optical properties, magnetism and excited states. Here we present some highlights from *Self-Interaction Correction: State of the Art and New Directions.*

## 1 Introduction and background

The thirtieth anniversary of the Perdew-Zunger paper [1] on the self-interaction correction to density functional approximations was the occasion for a celebratory conference, "Self-Interaction Correction: State of the Art and New Directions", held 19-21 September 2011 in Chester, England. The conference was organized by Zdzislawa Szotek, Leon Petit, and Martin Lueders of STFC Daresbury Laboratory and sponsored by the European Science Foundation, the Daresbury node of CECAM (directed by Walter Temmerman), and Psi-k. It ended with a round-table discussion moderated by Malcolm Stocks. This highlight will present some impressions of the subject and the conference. We attempt to provide a discussion on all subject matter touched upon at the meeting and to place that discussion within the context of papers published during the last three decades.

But first let's go back thirty years to 1981: The basic theorems of density functional theory (DFT) [2–4] were already established. These theorems permit a calculation of the ground-state density and energy of many electrons in the presence of a static external scalar potential, and thus a prediction of the structure of atoms, molecules, and solids, using fictitious one-electron wavefunctions or Kohn-Sham orbitals [3] that see a self-consistent scalar potential. In practice, the many-body exchange-correlation contribution to the energy as a functional of the density must be approximated, and the only approximation in use then was the local spin density approximation (LSDA) [1,3,5,6]

$$E_{xc}^{LSDA} = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{unif}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})), \tag{1}$$

where $\epsilon_{xc}^{unif}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy per particle of an electron gas with uniform spin densities. The exchange-correlation energy is a relatively small part of the total energy, but it is "nature's glue". Without it, bonds would be much longer and weaker than they actually are [7]. LSDA was exact by construction for uniform or slowly-varying densities, but it made serious errors (e.g., energies several eV too high) for the hydrogen atom and other one-electron densities. Thus density functional theory was already widely used in solid state physics, but hardly at all in chemistry [8]. The derivative discontinuity of the energy was not yet known. But it [9] and the generalized gradient approximation (GGA) [10–14]

$$E_{xc}^{GGA} = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{GGA}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \tag{2}$$

were almost ready to appear.

After 1981, two roads diverged in density functional theory. The road subsequently more traveled led from LSDA to GGA and higher-level semilocal functionals (meta-GGAs) [15,16] and eventually made DFT widely useful to chemists as well as solid state physicists. The road subsequently less traveled led from LSDA to the self-interaction correction (SIC) to the derivative discontinuity (and perhaps to the related LDA+U method [17]), and to a useful treatment of strongly-correlated materials such as transition-metal oxides, lanthanides, and actinides. Curiously, the strengths and weaknesses of these divergent approaches are complementary: The semilocal functionals can be accurate for *sp* bonds near equilibrium, while SIC can be accurate for open-shell *d* or *f* electrons or for any stretched bonds over which electrons are shared. Stretched bonds occur for example in the approach to the dissociation limit [9,18–20], and also at the transition states that determine the barrier heights for chemical reactions [21]. Perhaps these two roads can converge in a way that will retain the strengths and eliminate the weaknesses of each. But little of this was anticipated in 1981.

First separately [22,23] and then together [1,24], Perdew and Zunger proposed to make DFT exact for any one-electron density through an orbital-by-orbital self-interaction correction (PZ-SIC). Their comprehensive paper [1] has been cited over 9000 times, partly for SIC and partly for its parametrization of $\epsilon_{xc}^{unif}(n_\uparrow, n_\downarrow)$. It is the 8th most-cited physics paper of the past 30 years [25]. The conference organizers provided a birthday cake, with the first page of the paper printed on top, giving John Perdew and Alex Zunger a chance to eat their own words, along with the other participants.

## 2 SIC theory and its formal properties

The PZ-SIC [1] to any density functional approximation is

$$E_{xc}^{PZ-SIC} = E_{xc}^{approx}[n_\uparrow, n_\downarrow] - \sum_{\alpha\sigma}\{U[n_{\alpha\sigma}] + E_{xc}^{approx}[n_{\alpha\sigma}, 0]\}. \tag{3}$$

Here $\sigma = (\uparrow, \downarrow)$ is the quantum number for the z-component of electron spin, and $\alpha$ is the set of orbital quantum numbers other than spin.

$$n_{\alpha\sigma}(\mathbf{r}) = f_{\alpha\sigma}|\psi_{\alpha\sigma}(\mathbf{r})|^{\mathbf{2}} \tag{4}$$

is the contribution to the density from normalized orbital $\psi_{\alpha\sigma}(\mathbf{r})$ with fermion occupation number in the range $0 \leq f_{\alpha\sigma} \leq 1$ and

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) = \sum_{\alpha\sigma} n_{\alpha\sigma}(\mathbf{r}) \tag{5}$$

is the electron density. Finally

$$U[n] = \frac{1}{2}\int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{6}$$

is the Hartree electron-electron repulsion energy of density $n$.

PZ-SIC has several correct formal properties [1]. Although it is in a sense an *ad hoc* correction, it is hard to think of any similar approximation for the energy that satisfies so many correct constraints. (There are however reasonable alternatives for the SIC effective one-electron potential, discussed at the conference by Olle Eriksson [26], who focussed on the calculation of the electron density.) Here we will discuss only four correct formal properties, with the fourth only recently appreciated:

1. For any one-electron system in a state $\psi_{\alpha\sigma}$, $n_\sigma(\mathbf{r}) = n_{\alpha\sigma}(\mathbf{r})$ and $n_{-\sigma}(\mathbf{r}) = 0$ so

$$E_{xc}^{PZ-SIC} = -U[n_{\alpha\sigma}] \tag{7}$$

to properly cancel the Hartree energy $U[n]$. Thus PZ-SIC is exact by construction for any one-electron density.

2. Any self-interaction correction to the exact functional would be spurious. PZ-SIC seems to give no correction to the exact spin density functional $E_{xc}^{exact}[n_\uparrow, n_\downarrow]$, since

$$U[n_{\alpha\sigma}] + E_{xc}^{exact}[n_{\alpha\sigma}, 0] = 0. \tag{8}$$

   A subtlety here is that, in any system of more than two electrons, some real orbitals necessarily have nodes and are not one-electron ground states for any smooth potential (although they may be ground states for sufficiently singular potentials). We will discuss this further in Sec. 4.1.

3. In a single-center system such as an atom, the PZ-SIC orbitals could be very close to Kohn-Sham orbitals. But, in multi-center systems with the same Kohn-Sham potential on each center, the Kohn-Sham (canonical) orbitals become more diffuse as more centers are added. The PZ-SIC correction on Kohn-Sham orbitals would be non-zero for one atom, but zero per atom for a collection of infinitely-many well-separated identical atoms, and the SIC energy would not be size-consistent. To achieve size-consistency, the energy-minimizing SIC orbitals must localize around each center. This tends to be the case, at least when SIC is applied to LSDA, since in this case the correction tends to be more negative for a more localized orbital. Thus SIC steps outside the Kohn-Sham theory on which it is based. When applied to a uniform electron gas [27–29], the best situation for PZ-SIC-LSDA would be weak localization of the orbitals: weak enough to hardly change the LSDA bulk energy (correct for these densities), but not so weak as to produce a false surface energy (a kind of size inconsistency) [30]. We will discuss size-consistency again in Sec. 5.

4. $E_{xc}^{PZ}$ includes the full Hartree self-interaction correction,

$$-\sum_{\alpha\sigma} U[n_{\alpha\sigma}] \tag{9}$$

   as in Hartree-Fock theory and self-interaction-free Hartree theory, and in fact this is its only fully nonlocal term when $E_{xc}^{approx}$ is local (LSDA) or semilocal (GGA or meta-GGA). We will also discuss this correct formal property further in Sec. 2.5.

The orbitals that locally minimize the SIC total energy, subject only to the constraint of orbital normalization, are self-consistent solutions of the equation [1, 24]

$$[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + u([n];\mathbf{r}) + v_{xc,\sigma}^{approx}([n_\uparrow, n_\downarrow];\mathbf{r}) + \Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r})]\psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r}), \tag{10}$$

where $v_{ext}(\mathbf{r})$ is the external potential (typically the attractive interaction between an electron and the nuclei),

$$u([n];\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \tag{11}$$

is the Hartree electrostatic repulsion potential from the electron density $n(\mathbf{r})$, $v_{xc,\sigma}^{approx} = \delta E_{xc}^{approx}/\delta n_\sigma(\mathbf{r})$ is the Kohn-Sham exchange-correlation potential of the uncorrected approximation, and

$$\Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r}) = -\{u([n_{\alpha\sigma}];\mathbf{r}) + v_{xc,\uparrow}^{approx}([n_{\alpha\sigma},0];\mathbf{r})\} \tag{12}$$

is the SIC correction to the exchange-correlation potential. Up to this point, we use the same notation $\psi_{\alpha\sigma}(\mathbf{r})$ for all orbitals, but we shall later introduce $\phi_{i\sigma}(\mathbf{r})$ to distinguish SIC localized orbitals from canonical or symmetry-adapted orbitals. Originally Perdew and Zunger [1] were able to solve Eq. (10) only for atoms, where the SIC orbitals are necessarily localized and nearly orthogonal. These early tests suggested that PZ-SIC-LSDA was a nearly ideal approximation, with greatly improved total and ionization energies, more physical orbital energies approximating minus the electron removal energies, proper stability for negative ions [31], correct long-range behavior ( $-\frac{1}{r}$) of the exchange-correlation potential, etc.

## 2.1 Dissociation limit and fractional occupation

One can evaluate the total energy of an atom (or other many-electron system) as a function of the non-integer average electron number in it by using non-integer occupation $f_{\alpha\sigma}$ for the highest-energy partially-occupied orbital. Perdew and Zunger [1] observed that within SIC the total energy varies almost linearly between adjacent integer electron numbers, with slope changes at the integers. In contrast, within LSDA the total energy varies more quadratically, with small or zero slope changes at the integers. The smooth energy variation within LSDA was expected, on the basis of arguments by Slater [32], to lead to spurious fractional-charge dissociation of chemically-distinct atoms in most cases, an effect recently confirmed [18,33]. On the other hand, the piece-wise linear variation suggested by SIC leads to dissociated atoms that are properly charge-neutral.

Thus an approximation, PZ-SIC, led to the exact density functional theory [9] for an isolated open system of fluctuating electron number, in which the energy is exactly piece-wise linear between integer numbers. The nearly-correct behavior within SIC is now known to be what makes PZ-SIC useful for strongly-correlated systems, where electrons are shared between localized orbitals on different sites. And it is also known that property 4 in Sec. 2 is largely responsible for making PZ-SIC nearly many-electron self-interaction free in this sense.

Aron Cohen talked about the difficulty of achieving many-electron self-interaction freedom and accurate static correlation from the same approximate energy functional, using stretched $H_2^+$ and stretched $H_2$ as paradigm examples [34].

## 2.2 Localized and canonical orbitals

Molecules are much more challenging to SIC than atoms. Thus, thinking about applications to molecules allowed one to confront technical and conceptual challenges which arise in orbital-dependent functionals. The solutions of Eq. (10), which are nearly orthogonal in atoms, are no longer so in molecules. Pederson, Heaton and Lin [35, 36] (the Wisconsin group) found a way to implement PZ-SIC-LSDA for molecules, with the constraint of orbital orthogonality, and introduced the terminology of localized and canonical orbitals within PZ-SIC-LSDA [36–38]. The method was also used to determine slight improvements in atoms. An application of the variational procedure, with the constraint of orbital orthonormality, leads to the immediate conclusion that each of the orbitals which minimize the total energy does indeed move in an orbital-dependent Hamiltonian. However, the orthonormality constraints lead to a more complicated set of Schrödinger-like equations with a set of hermitian off-diagonal Lagrange multipliers coupling the states on the right-hand side of the equation. Several related questions raised within Ref. [1] or shortly thereafter in Refs. [35, 36] pertained to: (i) ensuring orbital orthonormality, (ii) ensuring hermicity of the Lagrange-multiplier matrix, (iii) determining which unitary transformation on a trial set of orbitals was best for constructing the SIC functional, and (iv) finding an interpretation for the Lagrange-multiplier matrix.

The physical answer to these riddles was alluded to by Perdew and Zunger in their original paper when they noted that the optimal orbitals for SIC might resemble the energy-localized orbitals of Edmiston and Ruedenberg [39]. Also, Harrison, Heaton and Lin had already demonstrated that Wannier functions, rather than, Bloch functions lead to self-interaction corrections in insulators of similar magnitude as found in atoms [40]. Following up on this hint, Pederson *et al* [35, 36] took a closer look at the variational procedure and determined that the orbitals which minimize the energy in orbital-dependent theories must also satisfy additional constraints given by:

$$[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + u([n];\mathbf{r}) + v_{xc,\sigma}^{approx}([n_\uparrow, n_\downarrow];\mathbf{r}) + V_{xc,i\sigma}^{SIC}(\mathbf{r})]\phi_{i\sigma}(\mathbf{r}) = \sum_j \lambda_{ij}^{\sigma}\phi_{j\sigma}(\mathbf{r}), \tag{13}$$

$$< \phi_{i\sigma}|V_{xc,i\sigma}^{SIC} - V_{xc,j\sigma}^{SIC}|\phi_{j\sigma} >= 0, \tag{14}$$

$$V_{xc,i\sigma}^{SIC}(\mathbf{r}) = -\{\int d^3r' \frac{|\phi_{i\sigma}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} + v_{xc\uparrow}^{approx}([|\phi_{i\sigma}|^2, 0];\mathbf{r})\}. \tag{15}$$

In the original work they suggested that a reasonable name for Eq. (14) was the localization equation since it rhymed, since it philosophically embodied earlier Hartree-Fock-based perspectives offered by Edmiston and Ruedenberg, and since orbitals that satisified this equation and minimized the total energies for the LSDA exchange-only functional tended to be localized. By 1986, Pederson had already wondered whether he should have called this equation the orbital optimization equation, a name that would have more aptly provided an umbrella for the discussion about intermediate range and complex orbitals at the meeting.

While the above equations first appeared as a departure from the normalization-only equations derived by Perdew and Zunger, it was realized quickly that, if the above equations were solved, a set of orthonormal eigenfunctions of the occupied-orbital Lagrange-multiplier matrix would satisfy an equation identical to Eq. [10] with a generalized nonlocal SIC potential defined according to:

$$\Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r})|\psi_{\alpha\sigma}> \rightarrow \Delta V_{xc,\alpha\sigma}^{SIC}|\psi_{\alpha\sigma}> = \sum_i M_{\alpha i}^{\sigma} V_{xc,i\sigma}^{SIC}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}). \tag{16}$$

In the above expression, the matrix $M_{\alpha i}^{\sigma}$ is a unitary matrix connecting the localized-orbital set $\{\phi_{i\sigma}\}$ to the so-called canonical orbital set $\{\psi_{\alpha\sigma}\}$. For example (assuming that the SIC correction to the energy is negative for the localized orbitals):

1. For molecules, the matrix $M$ in Eq. (16) connects symmetry-adapted molecular orbitals to orbitals that are qualitatively similar to those of Edmiston and Ruedenberg.
2. For atoms, the matrix $M$ connects *s, p* and *d* orbitals to hybridized orbitals.

3. For crystals, the matrix $M$ is simply the unitary matrix which connects Wannier functions to Bloch functions, but the Wannier functions will resemble the atomic localized orbitals (i.e. $M_{\mathbf{k}\mathbf{R}_\nu} \rightarrow \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}_\nu}$).

Chemistry and chemical physics are games of kcal/mole and any nonsystematic uncertainties due to the use of approximate local orbitals could significantly impact binding energies and barriers. Moreover the determination of ground-state geometries and critical points associated with transition states and reactant/product states essentially requires a capability for the treatment of Hellmann- Feynman forces which, in their derivation, require that all first variations are zero. If a new generation of scientists decides to navigate the "road less traveled" and seek a new rung of orbital-dependent SIC functionals, it is likely that such functionals will be more easily analyzed and constructed if full attention to the variational principle and localization equations is an integrated component during the development of the functionals. However, such a strategy was not historically possible.

## 2.3 Koopmans' theorem for SIC

The justification for arguing that it made sense to diagonalize the resulting Lagrange-multipler matrix came by proposing that of all (e.g., infinite number) the possible unitary transformations one can imagine, there is one unitary transformation that is best from the standpoint of simultaneously minimizing the energy of the N and N-1 electron states [36–38]. In this regard, one writes the occupation-dependent localized orbitals in terms of an alternative set of occupation-dependent orbitals and introduces the constraint that the latter set must lie in the space spanned by canonical orbitals of the N-electron system.

$$\phi_{i\sigma}(\mathbf{f}) = \sum_{\alpha} (U^{\sigma}_{\alpha i})^* \sqrt{f_{\alpha\sigma}} \psi_{\alpha\sigma}(\mathbf{f}). \tag{17}$$

It is then determined that the unitary transformation $U$ in the above equation that minimizes the energy for the N-1+f$_{N\sigma}$ is identically equal to the hermitian conjugate of the matrix M in Eq. (15).

This Koopmans-like argument generalized the original arguments of Perdew and Zunger and led to similar numerical results for atoms. However, it provides better approximations to ionization energies in delocalized systems where the lowest ionized state is generally achieved through the removal of a delocalized (canonical) rather than a localized electron. A lingering question that hopefully will be answered some day was raised in Pederson's talk: Will the generalization for constructing localized orbitals for non-integer systems always lead to fully occupied localized orbitals for integer systems? The propensity of SIC to variationally disallow fractionally occupied solutions to integer systems leads one to expect that an additional constraint is unnecessary, but some effort toward understanding that point would be useful.

We mention that a recent paper by Stengel and Spaldin [41] analyzed Janak's argument [42] within the context of an application of SIC to crystalline silicon. The authors considered the consequences of assuming that the occupation numbers are to be placed on Wannier functions. The authors noticed that Janak's theorem is applicable for each Wannier function but that this does not lead to a band structure. This statement is correct regardless of whether one is finding the Wannier functions that minimize the SIC-LSDA-based or LSDA-based energy functional. Here we reiterate that Koopmans' theorem [36–38] points directly to eigenvalues of the Lagrange multiplier matrix because it picks out the representation of wavefunctions that are most likely to minimize the ionized state and because, within SIC-LSDA, the non-Koopmans' corrections are small. Originally, Janak's theorem was tacitly aimed at the highest-occupied or lowest-unoccupied orbital in the LSDA method. Because of that assumption, the question as to whether or not the resulting derivative had an extremal property was not specifically addressed but seems to have been assumed. For example this theorem was used to argue that, in LSDA, the only fractionally occupied states could be at the Fermi level.

In retrospect, Koopmans' theorem for SIC is stating that the total derivative of the energy with respect to occupation number is equal to the partial derivative of the energy with respect to occupation number (Janak's theorem) if, for that occupation number, the energy is minimized with respect to every other possible variational parameter in the problem (i.e., all other partial derivatives are zero). In other words the Koopman's theorem is very similar to a Hellmann-Feynman theorem for occupation numbers. The original Koopmans theorem [43], for Hartree-Fock theory, is mathematically stronger as it does not rely upon derivatives of the N-electron state to estimate the energy of the (N-1)-electron state. However Koopmans' theorem for SIC includes correlation so it may be physically and chemically stronger.

The Wisconsin SIC group suggested several possible means for representing the nonlocal SIC potentials in terms of local potentials. Such approximations are fine if one is primarily interested in understanding spectra and band alignments, since these approximations allow for SIC calculations with complexity similar to LSDA. However in an era where gradient algorithms [44] and Car-Parrinello methods [45] have become a common means for solving the Schödinger equation, it seems that methods based upon iterative refinement of the localized orbitals are probably the best approaches. It was also evident at the meeting that the use of SIC had migrated into most types of electronic structure codes. Axel Svane discussed the implementation of SIC into the LMTO methods and described applications to *f*-electron systems. Eric Suraud [46, 47] presented interesting results on an SIC-based approach that is available in the Amsterdam density-functional codes. In this method one uses a common SIC potential for an N-electron system based upon the average orbital density ($n(\mathbf{r})/N$). For example when the method is applied to sodium clusters, the authors of Refs. [46, 47] find that the one-electron ionization energy computed using a total-energy difference agrees well with the highest-occupied orbital eigenvalue. The averaged SIC potential was approximated as:

$$\Delta v_{xc,\alpha\sigma}^{AVG-SIC}(\mathbf{r}) = -\{u([n/N];\mathbf{r}) + v_{xc,\uparrow}^{approx}([n(\mathbf{r})/N,0];\mathbf{r})\}. \tag{18}$$

Such an approach eliminates the need to solve localization equations, at the expense of a more approximate SIC potential. This approach provided good valence ionization energies and is also exact in the one-electron limit. In scheduled talks and informal discussions, the Icelandic group (Peter Klüpfel, Simon Klüpfel, Hildur Guðmundsdóttir, and Hannes Jónsson) shared their experiences with several different strategies for finding solutions to the SIC equations, including an early method due to Goedecker and Umrigar [48].

Another form of self-interaction correction [49–52] that was based on the use of pseudopotentials received a significant amount of discussion in the talks. In this approach, atomic corrections are performed to determine nonlocal, norm-conserving pseudopotentials which incorporate self-interaction corrections in a nonlocal *l*-dependent pseudopotential. Once this method is adopted, the nonlocality of the pseudopotential allows for the calculations of self-interaction corrections in condensed systems. Bjoern Baumeier described this method for calculations of electronic structures in solids. This method was used for calculations on a large number of compounds with partially ionic characteristics. Materials included silicon carbide and alkali-metal oxides. Calculated properties included electronic and atomistic structures and optical spectra. The method was also shown to be useful for the study of magnetic properties of dilute magnetic semiconductors. Alessio Filippetti discussed use of this approach for the study of strongly-correlated oxides. Hisazumi Akai discussed an approximate SIC method for the Kohn-Korringa-Rostocker methodology and provided a variety of applications. Stephano Sanvito also used this pseudopotential approach in his discussion on transport properties.

Nikitas Gidopoulos suggested a possibly unique way to turn an approximate Kohn-Sham potential into a self-interaction-free Kohn-Sham potential (multiplicative and orbital-independent) [53].

## 2.4 Spectra and excitations within SIC

The qualitative differences between SIC and SIC-LSDA are depicted in Fig. 1. The SIC pulls down the occupied states relative to the unoccupied states which generally leads to a gap ($\Gamma$) that is improved in comparison to experiment. Localized excitations in a vacuum or excitons in a wide-gap insulator (depicted as E) can be difficult to identify within LSDA calculations. In LSDA-SIC, with an approximation to the particle-hole interaction ($\delta$), the description of such excitations can be improved. For defects in solids, where localized levels occupy the gap, LSDA and GGA calculations tend to place the defect levels (labeled by $\Delta$) too close to, or overlapping, with the unoccupied conduction band. However, SIC-LSDA pulls the defect levels down and often places the LSDA-false-positive shallow levels (discussed in Alex Zunger's talk) in the proper location. With inclusion of SIC and a particle-hole interaction, an unoccupied continuum of defect levels, predicted by the Mott-Gurney theorem, begins to emerge [54]. Less consensus exists regarding the differences between SIC-LSDA and LSDA for charge-transfer excitations, but there are some examples that show LSDA can dramatically underestimate these energies and that an approximate self-interaction-corrected energy with a particle-hole interaction restores the correct asymptotic form for donor-acceptor and other charge-transfer excitations. For example, in a vacuum, these energies are found to be close to (I-A-1/R) [55,56]. For spin excitations, determined from LSDA/GGA derivations of Heisenberg Hamiltonians, a large number of calculations show that the spin-excitation energies are overestimated due to LSDA's tendency to slightly delocalize the *d*-electrons and since the kinetic exchange interactions depend exponentially on the localization of the *d*-electrons. Therefore inclusion or partial inclusion of self-interaction corrections lowers the spin-excitation energies (See Ref. [57] and references therein) and improves agreement with experiment. While not depicted in the picture, vibrational spectra [58,59] seem to be relatively well accounted for within LSDA and GGA. However, since polarizabilities are dependent on SIC [20], the Raman intensities are also expected to show some dependence on the

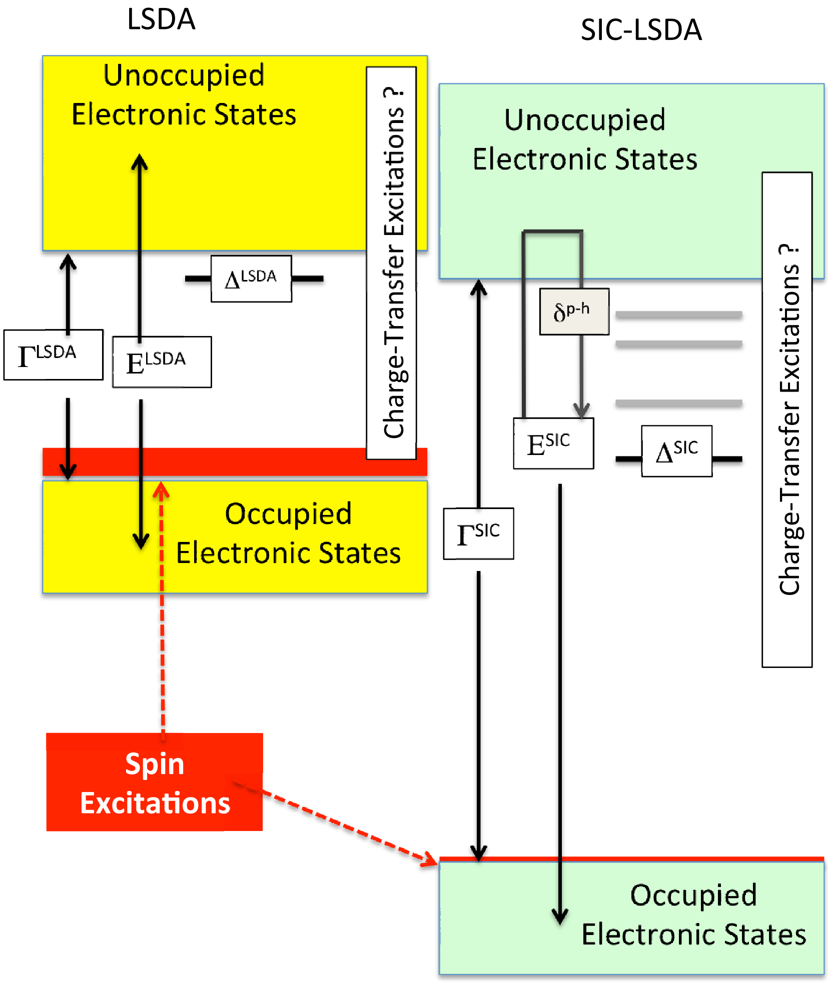

Figure 1: Schematic and qualitative picture depicting differences between LSDA (superscript "LSDA") and SIC-LSDA (superscript "SIC") energy levels. The behavior of the energy gap, excitonic states, and defect levels are depicted by $\Gamma$, $E$, and $\Delta$ respectively. The particle-hole interaction is depicted by $\delta^{p-h}$. The behavior of the very low-energy spin excitations are depicted in red (not to scale). There is some evidence that charge-transfer excitations are also improved within SIC-LSDA. SIC may be expected to decrease the occupied bandwidth in wide-gap systems and increase the occupied bandwith in gapless systems. The picture is expected to inform one's intuition and apply to many cases.

inclusion of self-interaction corrections. From this standpoint we note that Delugas, Fiorentini and Filippetti have found that dynamical charges are improved by approximately 15 percent in $LaAlO_3$ [60].

Exact accounting for the changes to the variational principle due to explicit orbital dependence is not likely to be of significant import from the standpoint of the calculation of electronic spectra. This seems to have been highlighted in the earlier works of Harrison *et al* [61] and in much of the *f*-electron calculations that have been led by Temmerman *et al* [62–64].

At the meeting Eric Suraud discussed the use of an average-SIC approach for the calculation of radiative transitions using the Amsterdam codes. Good agreement for valence ionization energies was obtained. Similarily Takao Tsuneda showed that a regional self-interaction correction seemed to give good agreement for core-level spectroscopy. Stephan Kuemmel discussed a means for determining the shape of the frontier orbital through the time evolution of the SIC-LSDA solutions, and compared SIC predictions to "measured orbital densities" [65]. Also in this talk, a summary of earlier SIC-LSDA work which addressed its relevance to energy and charge transfer was provided [66].

Julie Staunton discussed the calculations of magnetic properties within an *ab initio* method [67–69]. She provided a brief overview of the disordered local moment (DLM) method of Lueders *et al* for incorporating effects of strong electron correlations using a local-SIC formulation. Applications to the phase diagram of Gd were presented. Additional calculations on transition-metal oxides (MnO, FeO, CoO and NiO) were presented. These materials have anti-ferromagnetic order at low temperature, and the DLM-SIC approach explained the persistence of the large insulating gap into the paramagnetic state.

Molecular magnets [57, 70] represent another area where self-interaction corrections can be important, particularly in the Ni and Fe-based systems. For the $[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6Br_6]^{2+}$ molecule [70], density functional theory with the PBE-GGA functional describes the electronic structure of the molecular solid well, as evidenced by detailed comparison of the calculated optical spectrum with experiment. However, the HOMO-LUMO gaps are consistently underestimated and the calculations of the magnetic anisotropy Hamiltonian in this "$Fe_8$ molecule" are significantly less reliable than for molecular magnets composed of other *3d*-elemental centers [57]. The underestimation of the gap and/or the slight delocalization of the metal $3d$ electrons could be fixed through the inclusion of SIC and may provide more accurate calculations of spin-Hamiltonians and magnetic-anisotropy Hamiltonians.

Harrison *et al* [71] have presented empirical evidence that, for atomic excitations, one can determine excitation energies by allowing the unoccupied levels to move in the same SIC potential as the hole electron. A justification for this procedure based upon variationally optimized orthogonalized excited states has been offered for localized systems [54] and shown to provide very good quantitative results for F-centers in LiF. More recently Baruah and Pederson have extended these arguments to address a calculation of the charge-transfer excitation in a large molecular triad [55] composed of a $C_{60}$ molecule and a carotenoid organic chain that are tied together by a porphyrin chromophore. Without the explicit constrained variational procedure with orthogonalized ground and charge-transfer states, the LSDA-based charge-transfer excitation would collapse into a delocalized state with an energy that significantly underestimates experiment.

### 2.5 Bond energies and relation to GGA's

The GGAs, which started to appear in the 1980s, gave a much bigger improvement to atomiziation energies [10–12, 14] than PZ-SIC-LSDA did. GGAs, meta-GGAs [15, 16], and hybrids of these semilocal functionals with exact exchange made density functional theory popular in chemistry from the 1990s to the present. SIC was largely forgotten, except by a community of solid state physicists interested in studying strongly-correlated oxides (well-represented at the conference) and by a few chemists, e.g. [72–75].

In 2004-2005, Vydrov and Scuseria [76, 77] implemented a version of self-consistent PZ-SIC-LSDA with orbital orthogonality into a developmental version of the Gaussian code. They then applied it to a large test set of molecules. They found that the energy barriers to chemical reactions (stretched-bond situations) were improved significantly over LSDA, as Patchkovskii and Ziegler [21] had found before. But the results for equilibrium properties were disappointing: Atomization energies were only slightly improved over LSDA, and bond lengths were actually worsened.

One might expect better results from applying PZ-SIC to more sophisticated semilocal functionals like GGA or meta-GGA, but the opposite is found. Vydrov *et al.* [78] argued that GGAs and meta- GGAs improve $E_{xc}$ over LSDA for smooth, nodeless densities, but not for oscillating and noded orbital densities, where the relative density-insensitivity of LSDA may actually be an advantage. They also proposed a scaled-down SIC that is still exact for all one-electron densities but scales down the self-interaction correction in many-electron regions. They found that this improved equilibrium properties over the original PZ-SIC, but worsened stretched-bond properties. By losing the correct formal property 4 of Sec. 2, they also lost the correct many-electron self-interaction freedom [19, 79], retaining only one- and two-electron self-interaction freedom [19].

## 3 SIC for localization-delocalization transitions in solids and molecules

The explicit appearance of the orbital densities in the SIC formalism provides for greater computational challenges but also provides a richer space of physical and chemical solutions. The richness or multifaceted solutions offered by the inclusion of SIC were highlighted in several talks at the meeting. Alex Zunger's title, abstract, and talk succinctly, precisely and humorously framed the problem. Alex referred to the systematic exaggeration of delocalization as one of the primary "tragedies" faced by DFT practitioners. He spoke of this problem in terms of defects in insulators, particularly in regard to ZnO and GaAs, and the challenge of polarons [80, 81]. He expressed hope that a functional that could reproduce the near-linear dependence on occupation number that is found in SIC-LSDA could enhance further joint collaborative efforts between experimentalists and theorists. Other early works that talked about the important role of self-interactions in defect calculations include [82] and [54]. Here we provide an account on other manifestations of this issue.

## 3.1 Actinides and materials containing *f*-electrons

Axel Svane discussed his collaborative work with the Daresbury group on the calculation of phase diagrams of SmS systems [62]. Svane showed for a variety of systems that SIC provided a mixed picture, with some electron states being localized and some being itinerant. Such spectacular phase transitions are observed in cases like elemental Ce, CeP, SmS, and YbS. In actinides this delocalization phenomena proceeds by delocalizing the *f*-electrons one at a time, and the volume range over which the transition from the localized to the itinerant scenario can be identified

As a function of pressure, the partially filled *f*-shell must be handled carefully in these systems, as nature can be indecisive about the number of *f*-electrons that should be fully occupied within the atomic region of the Sm. Axel Svane showed that, depending upon volume, the Sm could accommodate either five or six *f*-states and that SIC succeeded in determining the parts of volume-space that preferred five rather than six electrons. The conclusion is that the SmX compounds require the self-interaction corrections to describe the filling of the *f*-shell as a function of unit-cell volume. The calculated SIC phase diagrams of SmS and SmAs compounds are found to be in quantitative agreement with experiment. For the high-pressure phase the results show that the sixth electron is itinerant and chooses to distribute itself amongst the remaining band of partially occupied *f*-states near the Fermi level. The itinerant states have no SIC. In contrast, the lower-density phase has a total of six *f* states occupied below the Fermi level.

Klaus Capelle discussed a means for testing the limitations of DFT through the use of model hamiltonians, and tested several versions of SIC within the Hubbard model [83].

## 3.2 Free-electron gas: dense metallic states and dilute "insulating" states?

As discussed in Refs. [27–29], there have been several different attempts to find localized orbitals for the free-electron gas. Most of the work discussed in these references was in regard to the standard free-electron gas which leads to a set of occupied plane-wave states inside a Fermi sphere. However in Ref. [29], Pederson, Heaton and Harrison also considered a phase of the free-electron gas that was much earlier considered by Wannier when he introduced the functions which bear his name [84]. It is interesting to note that, while Wannier was discussing plane-wave states, the title of that paper was *Structure of Electronic Excitation Levels in Insulating Crystals*. In this paper, Wannier wrote down Wannier functions of the form:

$$\omega(r - R_\mu) = \frac{1}{\sqrt{\pi^3}} \Pi_i \frac{sin[q_F(x^i - X^i_\mu)]}{\sqrt{q_F}(x^i - X^i_\mu)}, \tag{19}$$

with $\mathbf{R}_\mu = (m_x, m_y, m_z)(\pi/q_F)$ and $q_F$ is half the width of the cubic Brilloun zone. By inscribing the largest possible "Wannier cube" ($q_F = \frac{k_F}{\sqrt{3}}$) within the Fermi sphere, a set of Wannier functions may be derived. This set of functions leads to a negative self-interaction correction for about 37 per cent of the plane-wave states. This leads to a slightly wider occupied density of states which is in better agreement with Hartree-Fock theory. By inspection, and related to the uncertainty principle, it is clear that the original Wannier functions get more localized as the magnitude of the $q_F$-vector gets larger.

To frame the part of the paper on the insulating free-electron gas within the context of localization-delocalization transition, we again mention that the Daresbury-Aarhus group has successfully accounted for a high-density to low-density phase transition using SIC. The explanation appears to be that one can fill the Brilloun zone in two different ways. In one case it is possible to transform to six localized orbitals per site and in the other case only five. Now if one creates a "Wannier cube" that is large enough to accommodate all the electrons, $q_F$ gets larger and the Wannier functions become more localized. In addition to the fact that the Wannier functions are more localized, there are now 2.72 times as many localized orbitals. In a nutshell, Ref. [29] put forth the hypothesis that in the low-density limit, despite the large increase in kinetic energy associated with a non-spherical Fermi surface, the derivative of the energy with respect to $n^{1/3}$ is more negative in the limit of $n = 0$ (if the SIC-energy is indeed negative as is the case for the LSDA exchange-only functional). It was shown analytically that, in the low-uniform-density limit, a state that is based on a full band of plane waves/Wannier functions confined within a simple-cubic "Wannier cube" is lower in energy than the standard state composed of plane waves confined to the Fermi sphere. Pederson also speculated that this feature could be related to the Wigner crystallization and estimated that for values of $\mathrm{r}_s > 35$ the uniform density "insulating state" (plane waves within a "Wannier cube") are lower than the metallic state. That paper noted that "the subject of SIC-induced Wigner crystallization of the free-electron gas and antiferromagnetic- paramagnetic transitions in monovalent metals will be explored in a forthcoming paper", but it has not yet appeared. However in retrospect, it may be very important to ascertain whether there are indeed two quantum-mechanical phases of the uniform electron gas corresponding to two different Brilloun zones and two different density regimes. Knowing this may very well determine if the sign of the SIC-energy of a localized orbital in the low-density limit must be negative. The fact that numerous Brilloun zones (beyond those of Refs. [27–29]) exist means the estimate above is just that.

Based on experience with finding the SIC-LSDA antiferromagnetic solutions in the separated-atom limit for $\mathrm{Li}_2$ [36] molecules, Ref. [29] also mentioned the possibility of finding transitions between antiferromagnetically-ordered and paramagnetic states in monovalent metals, which is related to the discussion of BCC hydrogen presented by Thomas Schulthess. Consensus on what SIC predicts in the exchange-only limit and with correlated functionals for the free electron gas and monovalent n-dimensional systems could provide insight on which path toward improving SIC is likely to be most useful.

### 3.3 BCC hydrogen

Thomas Schulthess discussed attempts at understanding the localization-delocalization transition in BCC hydrogen and NiO within full-potential methods. For example in very early work by Svane and Gunnarsson [44], it was demonstrated that SIC-LSDA found a metal to antiferromagnetic transition at $r_s = 2.45$. Particular emphasis was on a description for addressing BCC hydrogen and metal-oxides using an implementation of SIC in a LAPW-based method. The previous LMTO-ASA-based investigations [44, 85, 86] were found to be in accord with the results of this more accurate methodology.

## 3.4 Geometries of radicals

The self-interaction error can also be the cause of qualitatively incorrect structures in organic radicals. For example, very recently Oyeyemi *et al.* [87] have demonstrated this in calculations on the alkynyl radical structure. In this work they demonstrate for a large range of functionals, including hybrids, that the self-interaction error causes an erroneous electron delocalization which induces a rehybridization of the valence electrons and ultimately causes a qualitatively incorrect structure of the radical (bent when it should be linear). Ramifications of such qualitatively incorrect structures then lead to quantitative thermochemical errors.

## 3.5 Polarizabilities, charge separation and transport

LSDA, GGA, and other semilocal functionals can fail to describe processes in which electrons are transfered over long distances, even in the ground state. Failures in the dissociation limit have aleady been discussed in Sec. 2.1. The semilocal functionals also overestimate the static polarizabilities, and even more the static hyperpolarizabilities, of molecules, especially for long molecular chains with stretched bonds between the atoms. These errors are largely corrected by PZ-SIC-LSDA [20]. In this reference, the longitudinal polarizabilities were calculated within high-level quantum-chemical methods, with both local and gradient-corrected functionals, and with self-interaction-corrected local and gradient-corrected functionals. The results show small (at most 20 percent) variation between all methods for small $H_2$ chains but large (50 percent) errors for a chain of six dimers when one compares DFT approximations to any method that accounts for the self-coulomb interaction in some way (e.g., SIC, CCSD, HF, MP4). Such a spurious propensity toward DFT-based dielectric breakdown is a very fundamental issue that is relevant to charge transfer, donor-acceptor systems (especially when in solvents), and molecular electronics.

Nicola Marzari provided a frank and provocative assessment on problems related to localization-delocalization transitions. He commented on the need to include self-interaction corrections and a generalized Koopmans relation [88] to improve the description of a variety of fundamental processes relevant to energy applications. Specific examples mentioned in his talk included charge-transfer excitations, photoemission spectra, and the structure and reactivity of transition-metal complexes. Also related to the proper dissociation of ionic molecules are questions related to simulation of charge transfer that are important for understanding photo-driven solar collection processes and simulation of molecular electronics. Sanvito discussed the prospects for improving the simulation of molecular electronics at the meeting.

Sanvito's contribution discussed the most common pitfalls in the non-equilibrium Greens function (NEGF) DFT approach to electron transport, and demonstrated that an approximate self-interaction correction could be used to obtain quantitative predictions for technologically relevant nano-scale devices. Examples concentrated on transport in molecules, in multi-functional tunnel junctions, and in organic systems in solution.

## 3.6 Technical details

There is an important technical feature, that received significant hallway discussion, on the use of the unified Hamiltonian and the analysis of the results. We attempt to reproduce that discussion here, as this, and actually all other iterative approaches which successfully minimize the SIC energy, may tempt one to conclude that there are in fact multiple orbital sets and multiple band structures which lead to the exact same total energy and the exact same density. To discuss this in the most efficient manner, it is easiest to first consider the case where the SIC happens to be zero, which would lead to a use of the unified Hamiltonian for a DFT Kohn-Sham calculation. Within density-functional theory, it is easy to verify that unitary transformations on the Kohn-Sham orbitals will allow one to determine an infinite number of orbitals sets that have different nondiagonal Lagrange-multiplier matrices but lead to the same total energy and the same total density. For simplicity we first consider any one of the equivalent sets of DFT orbitals that lead to a set of diagonal elements of the Lagrange-multiplier matrix that are nondegenerate. Using any one of these sets of DFT orbitals for construction and subsequent diagonalization of the unified Hamiltonian will allow us to re-extract the equivalent set of orbitals and the diagonal elements of the Lagrange-multiplier matrix for this set. Of course this set does not agree with the eigenvalues of the DFT Hamiltonian. However diagonalizing the Lagrange-multiplier matrix for this set of orbitals or any other set of unitarily equivalent orbitals will give the exact KS orbitals and the exact KS eigenvalues. Thus even for DFT, if a unified Hamiltonian is used, it is always necessary to diagonalize the Lagrange-multiplier matrix to compare results from different computer codes or users. Different starting points in the iterative procedure will lead to different, but unitarily equivalent, Lagrange-multiplier matrices even for density-functional theory. To the extent that this should happen for DFT, it should not be surprising that orbital-dependent functionals can also converge to different, but unitarily equivalent, Lagrange-multiplier matrices. This is simply a correct aspect of the minimization procedure.

## 3.7 Bandgaps and localized excitation energies

In insulating and semiconducting solids, LSDA, GGA and meta-GGA orbital energies yield fundamental band gaps that are smaller than experimental values associated with excitation of an electron to the lowest-lying conduction state. It has been argued [89, 90] that, because of the derivative discontinuity, a similar underestimation could occur in the exact Kohn-Sham bandstructure for the neutral solid, in which all electrons see the same multiplicative orbital-independent effective potential. When the electrons are tightly-bound, as in solid Ne, the gap in the exact Kohn-Sham band structure may more accurately approximate the first exciton energy.

From the standpoint of comparing results for the occupied orbital space, it is clear that one needs to compare eigenvalues of the Lagrange-multiplier matrix and that the associated eigenfunctions will generally exhibit the point-group and/or translational symmetry of the system in question. However a standard means for comparing unoccupied states may need to be established. The purpose of this section is to provide a discussion on past treatments of unoccupied states in SIC, without claiming that any of these treatments are necessarily rigorous when compared to more modern approaches to excited states. Such a discussion is useful from the standpoint of developing a standard means for comparison, especially since different methodologies treat the unoccupied states differently. Historically, there were efforts aimed at improving band gaps by allowing the delocalized occupied states to move in their standard SIC potential according to Eqs. (13-17), and to take the point of view that the unoccupied states should simply move in the LSDA hamiltonian. Since a delocalized electron outside a closed shell will have an LSDA eigenvalue that is an excellent approximation to the electron affinity, one may argue that the lowest unoccupied bloch function in a crystal should be a good approximation to the inverse photoemission experiments. Moreover, the Koopmans' theorem tells us that the energy to remove a delocalized electron from the crystal is approximately equal to the highest-occupied eigenvalue. Therefore, at least for ionic insulators, we expect that the eigenvalue differences will agree with SIC-LSDA total energy differences and form a reasonable approximation to one idealization of the experimental band gap. Further it is known that the resulting "scissored" bandstructure when compared to experiment is improved over LSDA [40, 41, 49, 91]. Note that the SIC of a delocalized electron is zero so it will not affect the estimate of an affinity. For lack of a better terminology we refer to this as the SIC insulating bandgap approach (SIBA).

In atoms [61], F-centers [54], other defects [82], core-level-excitations, and (presumably) localized excitons, there is good numerical evidence that one can obtain relatively accurate excitations by allowing the lowest unoccupied "particle" state to move in the same SIC-potential as the "hole" state. Arguments have been made as to why that should be expected [54]. So, for localized excitations and delocalized excitations in wide-gap systems, these two different treatments of the unoccupied states could be used as a basis for comparing SIC results that have been generated using different implementations. Simply examining these approximations will also allow practioners to develop some intuition on what types of interactions are required for better qualitative treatments of excited states.

The more difficult question is to determine a means for comparing gaps in strongly covalent systems. In Ref. [38], Pederson, using the methods described in [92], found, using SIBA, that the resulting silicon bandgap would be overestimated significantly since the SIC shift of a silicon 3s or 3p function (in an atom or in a crystal) is approximately 3.52 eV. If a SIBA picture is adopted, this would lead to a bandgap of approximately 4.22 eV which is in good agreement with the recent calculations of Stengel and Spaldin who find a value of 4.5 eV. [41]. However, in Ref. [38], Pederson argued that one should not expect the SIBA treatment to work for systems, such as silicon, where the excitonic levels lie above the onset of the conduction band.

## 4 Possible directions for further improvement of SIC

The Perdew-Zunger SIC has had both striking successes and striking failures, as summarized in the preceding sections. "How can anything so right be so wrong?" It is hard to see how to change the form of PZ-SIC without losing at least some of its formally correct properties. But there are two other possibilities that might work together:

## 4.1 Complex localized orbitals for SIC

PZ-SIC might work much better, and might improve along with the functional $E_{xc}^{approx}$ being corrected, if we could replace the oscillating and noded orbital densities by smooth, un-noded densities. (See point 2 of Sec. 2.) While real orbitals that are orthogonal must have noded orbital densities, complex orbitals need not. For example, plane waves are complex, orthogonal, and have constant orbital densities. Their real and imaginary parts have nodes, but not in the same places. Can we start from real canonical (delocalized) orbitals, then make a unitary transformation [35, 36] to localized complex orbitals that lower the SIC total energy more than localized real orbitals do? At the SIC workshop, John Perdew argued that such a transformation might represent a formal improvement to PZ-SIC, while Peter Klüpfel and collaborators demonstrated such a transformation for use in GGA [93].

From a technical point of view it should be noted that the localization equations are ambivalent toward changing the real and imaginary parts of a set of orbitals that already satisfy the localization equations. In other words, if one finds a set of real localized orbitals, an infinitesimal 2x2 complex unitary transformation would not change the energy to first order. So once a set of real localized orbitals are found, one is trapped in that orbital set. To escape that set and consider other possible solutions of the richer space of chemical and physical solutions requires the user to guess a different set of localized orbitals and determine if other local minima provide better estimates to the global SIC state. Alternatively one could consider second derivatives of the localization equations, which are not necessarily zero, to provide insights about whether a set of orbitals corresponds to a global minima. In the absence of an SIC functional for the exchange-correlation term, the second derivatives would provide easily calculated coulomb integrals and essentially determine which set of Edmiston-Ruedenberg orbitals provided globally stable solutions. However the intrinsically non-quadratic behavior of the exchange-correlation part of the functional makes it difficult to gain further insight through such analysis. Kuemmel, during his talk, commented that the time-dependent evolution of the SIC equations, which provides a means for minimizing the energy, necessarily considers the possibility of complex orbitals. Perhaps this approach to orbital localization allows one to circumvent the possibility of being trapped in real solutions or to confirm their global stability.

Additional guidance may be found by reviewing earlier work on atoms that grappled with similar issues on simpler systems. In applications to atoms, Harrison [71] discussed the use of spherical-harmonic $p$-orbitals and cartesian $p$-orbitals for construction of the SIC potential, and referred to this as Central-Field Self-Interaction Correction (CFSIC). For Ne, Harrison's work showed that the spherical-harmonic (complex) $p$-orbitals produced an SIC correction to the total energy that was approximately 2.7 eV lower than the cartesian representation. Further support that a set of complex nodeless wavefunctions would provide more negative SIC energies comes from a wealth of data showing that sphericalized densities lead to even larger (more negative) SIC corrections to the energy. However in Ref. [37], it is shown that by allowing $s$-$p$ hybridization, referred to as hybridization-localization (HL), the real $sp^n$ hybrids always delivered lower energies for the first 18 atoms in the periodic table. For neon the real HL solution is about 6.0 eV lower than the complex CFSIC solution. Still there is yet one more unpublished "however": For the SIC functional and numerical schemes used in Ref. [37], Pederson's recollection is that a brute-force determination of the SIC energy using a large series of 2x2 complex unitary transformations on the entire orbital space (*1s, 2s, 2*$p_x$, *2*$p_y$, *2*$p_z$) did indeed produce complex orbitals with energies slightly lower than the $sp^n$ hybrids.

### 4.2 Higher *l* hybrid orbitals

In addition to considering the possibilities of complex localized orbitals, Pederson suggested that, especially for applications which include *f*-electrons, localizing transformations achieved by "bonding" and "antibonding" combinations of *f* and *d* functions (real or complex) need to be considered. Since hybridization of states of different angular momentum and particularly parity occurs naturally in molecular bonds, it immediately follows that ignoring the possibility of localized atomic orbitals that are mixtures of different angular momenta is susceptible to overestimates of the actual SIC bond energies. Interestingly, in applications to the Zn$^{2+}$ cation, Stengel and Spaldin suggest that nine nearly similar $sp^3d^5$ hybrids could be the best localized orbitals [41].

## 5 Perspectives

It is also possible that further improvement of GGAs or meta-GGAs could make them work better with PZ-SIC. Orbital densities typically have larger reduced density gradients than total densities do, so they sample more of the large-reduced-gradient behavior of a GGA or meta-GGA. Standard GGAs and meta-GGAs may not be optimally constructed for this sampling. Indeed, the Icelandic group found failures of size-consistency for PZ-SIC applied to the Perdew-Burke-Ernzerhof GGA [14], arising from the strong large-reduced-gradient exchange enhancement over LSDA exchange that makes the PZ-SIC energy correction positive for some localized orbitals. (See point 3 of Sec. 2.) This strong enhancement also leads to an incorrect behavior under non-uniform density scaling to the two-dimensional limit [94–97], so fixing the latter problem might also fix the former. Diminishing the exchange enhancement factor (but in a different way) has already improved GGA [98–100] and meta-GGA [16] performance for solids. Note that many meta-GGA's including [16, 17] are already self-correlation free, so for them one can replace $E_{xc}^{approx}$ by $E_{x}^{approx}$ in the SIC correction term of Eq. (3).

Perhaps a convergence of "the road more traveled" with "the road less traveled" would provide an optimal unified nonempirical solution for the problems of "weak correlation" and "strong correlation". The hybrid functionals [101–104] that mix fractions of semilocal and exact exchange achieve this to some extent, but not fully and with the help of one or several more-or-less empirical parameters. Or perhaps the solution will come from a combination of the full exact exchange energy with some compatible nonlocal correlation energy functional, constructed using the exact exchange energy density and the sum rule on the correlation hole around an electron, as discussed at the conference by Adrienn Ruzsinszky. Such methods would appear to keep the important corrections for self-interaction error but leave the computational complexities of the localization-equation-induced undergrowth behind.

Robert Frost was known to warn his audience that *The Road Not Taken* is a "tricky poem" inspired by a hiker's concern that there was always a potentially better path to try. Unlike quantum particles, quantum physicists can not try all paths. It is expected that the optimal combination of the "road less traveled" with the "road more traveled" will in itself present many more different and exciting paths to explore and that the analysis leading to that optimal combination may be as tricky as the analysis of the poem. However, if scientific citation statistics [1, 25] are a guide, the end of this chapter should read:

I shall be telling this without a $\Psi$
Somewhere ages and ages hence:
Two roads converged in a green wood, and why?
This made the one best traveled by,
And that has made all the difference. *[sic]*

## 6 Acknowledgments

JPP acknowledges support from the National Science Foundation under Grant No. DMR-0854769 and under Cooperative Agreement No. EPS-1003897 with support from the Louisiana Board of Regents. Both authors thank the organizers, speakers, and participants for an interesting and stimulating conference. MRP thanks Prof. Chun C. Lin for providing the requisite "initial conditions" for part of this workshop report which allowed him to collaboratively focus on a hard and relevant problem for four stimulating years. The discussion does not necessarily represent the priorities of any government agency.

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