Research Networking Programmes

Science Meeting – Scientific Report

The scientific report (WORD or PDF file - maximum of seven A4 pages) should be submitted online within two months of the event. It will be published on the ESF website.

Proposal Title: *19th ETSF Workshop on Electronic Excitations: Complex systems in Biology and Nanoscience*

Application Reference N°: 5238

Summary (up to one page)

The 19th ETSF Workshop on Electronic Excitations was held at the University of Zaragoza, Spain, from the 23rd to the 26th of September 2014. The 2014 edition focused on the use of theoretical spectroscopy to describe complex systems in biology and nano-science. In this Workshop we brought together leading experts from different theoretical methods, computational implementation and experimentalists to identify current shortcomings in theoretical description, discuss improved numerical algorithms and implementation strategies, and ultimately combine different approaches to take advantage of the strengths of each one.

The sections were introduced by invited talks, experimental and theoretical. In total, there were 8 invited talks (speakers from Europe: France, Belgium, Switzerland, Spain, Italy; and the USA) and 26 contributed talks. The poster session has been held on the Wednesday afternoon, counting about 30 contributions. Both genders were well represented in our workshop: we had 3 (over a total of 8) invited talks and 12 (over a total of 26) oral contributed talks from female speakers. The workshop was attended by more than 80 participants, which allowed for fruitful scientific discussions among experienced and young researchers. In particular, the participation of young researchers was actively encouraged by keeping the fee relatively low and by selecting outstanding contributions for oral presentations.

Description of the scientific content of and discussions at the event (up to four pages)

In the following, we give a description of the scientific presentations ordered by thematics rather than chronological order.

Electron Dynamics

Electronic excitations and electron dynamics can often be very well described by time-dependent density functional theory. However, among the failures is the description of charge-transfer excitations which are only systematically included if one uses non-adiabatic functionals, i.e. includes the memory dependence properly. **N.T. Maitra** discussed the dynamics in strong and weak laser fields including a specific charge-transfer excitation which can be described with adiabatic approximations. Some detailed applications of adiabatic approximations were then discussed in two contributed talks (J.I. Fuks and J. Jokar). A further session on the theoretical foundations of density functional theory was started with the invited talk by **A. Abedi** on correlated electron-nuclear dynamics. He discussed the possible separation of the combined nuclear-electron wave function into an electronic and a nuclear part while still going beyond the Born-Oppenheimer approximation. The correlation of the electrons themselves was discussed by N. Helbig in a contributed talk showing a combination of density and reduced density matrix functional theory.

Many body perturbation theory

As one of the cornerstone methods within the ETSF network, many body perturbation theory methods were also this year the topic of a significant amount of presentations. The presence of new method development, systematic benchmarking and application to challenging problems made for two lively discussed sessions. The method developments discussed contained: large system/many cpu scaling improvements (X. Blase), the inclusion of electron—phonon coupling into the MBPT framework (C. Faber), high—throughput method for GW (M.J. van Setten), the ad-hoc construction of hybrid functional from GW calculations (M. Gerosa), and the calculation of effective masses from density functional perturbation theory with GW corrections (J. Laflamme Janssen). The benchmarking presented was mainly focused on molecular systems. **X. Blase** presented as part of his invited talk a comparison of GW+BSE to exCC3 on a set of fluorescent dyes. A general set 100 molecules for benchmarking GW with calculation using three different codes was presented by M.J. van Setten. The applications addressed included donor-acceptor complexes relevant for organic solar-cell technology (X. Blase) and wide gap

oxide surface systems in their application in the energy technologies of solar cells and photo-catalytic water splitting (M. Gerosa).

Ultrafast dynamics

The first-principles description of the time evolution of the electronic structure of molecules subject to ultra-short (attosecond timescale) strong optical pulses has been the subject of the contribution by F. Remacle and M. Verstraete.

The invited talk by **F. Remacle** focused on the modelling, mainly via time-dependent quantum chemical approaches, of pump-probe photonization experiments in the pre Born-Oppenheimer regime. Her studies on different molecules, form the small lithium hydride to the medium sized PENNA or tetrapetides, showed how it is possible to induce and probe charge transfer dynamics by means of attosecond pulses in different frequency ranges (from infrared to extreme ultraviolet). Precurring state of the art experiments, Remacle showed that attosecond pulse trains acts as frequency filters for molecular response, allowing the disentanglement of quantum beatings, generated by a previous infrared pulse, between states matching specific resonance conditions.

M. Verstraete complemented the previous talk by presenting a collaborative study aimed at benchmarking time dependent density functional theory against reference quantum chemical approaches (CAS and CCSD). By taking the lithium hydride molecule as a model system, he showed that the comparison between the two approaches is broadly satisfactory, highlighting at the same time some limitations of density functional theory. The insights brought by these results are expected to contribute to the design of improved functionals, by suggesting viable strategies to incorporate memory effects in time dependent simulations. Both talks stimulated vivid discussions, reflecting the timeliness of topic of attosecond electron dynamics and of the related open challenges for theory.

C. Rozzi (invited) reported about his recent work on the description of charge transfer in the excited states in donor-acceptor complexes, such as a covalently bonded light-harvesting system and polythiophene-fullerene blends for photovoltaic applications. These simulations, based on time-dependent density functional theory and Ehrenfest nuclear dynamics, shed light on early steps of charge separations, in which nuclear dynamics plays a key role in triggering charge delocalization and transfer, as also confirmed by time-resolved spectroscopy measurements. The talk was followed by a participated discussion, covering the implications of these findings and methodological aspects about the adequacy of density functional theory in describing charge transfer.

Electron transport

A session of the Workshop was dedicated to the investigation from first principles of quantum electron transport in nanosystems. S. Kurth proposed an accurate approximation to the dynamical xc correction in terms of the derivative of the xc potential of static DFT. He discussed how the discontinuity of the exchange-correlation (xc) potential is not only crucial to obtain an accurate Kohn-Sham conductance but also required to correct it towards the true, physical conductance. S. Dubois has discussed the use of the linear-scaling optimal basis density-matrix minimization (OBDM) approach for electron transport calculations and tight-binding parameters extraction. A. Neroni has used the embedded Green function approach to investigate the transport properties of multiferroic tunnel junctions.

Spectroscopy of biological systems

One session of the workshop was dedicated to large biological molecules, their spectroscopical signatures, and how to compute them from first principles. **Milagros Medina,** from the hosting BIFI Institute, was the experimental researcher chosen in this workshop to present her work: "Flavoproteins and Flavoenzymes: use of spectroscopy in the elucidation of action mechanisms". Although the ETSF workshop is obviously dedicated to theoretical spectroscopy, it is traditional in this series of events to invite one or more experimental experts. Prof. Medina presented results on numerous experimental techniques (absorption, fluorescence, circular dichroism, etc.) on flavoenzyimes and flavoproteins. Also, she discussed the current input that experimentalists get from first principles experts, and what are the requirements of calculations from an experimentalists point of view. The session was completed with the contributed talks from Anna Pikulska and Victor Moron, who presented computational work on excited states structures and circularly polarized luminiscence of biologically relevant chromophores (Pikulska), and fluorescent proteins (Moron).

Molecular Dynamics: Ivano Tavernelli (EPF Lausanne, Switzerland).

In this workshop, the topic of first-principles molecular dynamics was covered by the presentation of one of the invited speakers, Ivano Tavernelli "Nonadiabatic dynamics with relativistic effects using time-dependent density functional theory". Prof. Tavernelli is a leading experts in the application of surface-hopping techniques to tackle non-adiabatic effects from first principles. The presentation, besides the theoretical foundations of the approach, focused on relativistic effects (spin orbit couplings in the TDDFT framework), which are essential in the simulation of nonadiabatic transitions and inter-system crossings between potential energy

surfaces with different spin multiplicities. Some examples of application to the ultrafast excited state dynamics of transition metal-containing complexes were shown.

Large scale simulations

Joost VandeVondele, "Large scale simulations with DFT: GGA and beyond"

One of the main topics of the Workshop was devoted to the modeling of very large systems (hundreds or thousands of atoms) from first principles. The invited talk of J. VandeVondele discussed how the removal of all non-linear scaling steps from GGA DFT calculations and the development of a massively parallel GPU-accelerated sparse matrix library make structural relaxation and time propagation possible for systems containing 10'000s of atoms. In particular, he discussed a well parallelized implementation of a novel algorithm to compute four center integrals over molecular states (RI-GPW) allows for many-body perturbation theory (MP2, RPA) calculations on a few hundred atoms. Finally, he presented the application of these methods to liquid water and polarons in TiO2, as well as their implementation the freely available CP2K program.

H. Huebener has shown how the self-consistent Sternheimer method can be used to compute efficiently the optical excitations of large systems. The performances of a recently developed GGA exchange functional were presented by V. Vlcek. The electronic and magnetic properties of graphene/multiferroic interfaces were addressed by Z. Zanolli and, finally, the problem of exciton dispersion in layered materials was discussed by G. Fugallo.

Assessment of the results and impact of the event on the future directions of the field (up to two pages)

The ETSF workshop is the yearly opportunity to test and advance the current status of research in theoretical spectroscopy. Developers and users of the most used packages for theoretical spectroscopy meet and discuss new developments and challenges. This edition has been no exception. We had a wide overview of the numerous techniques that are nowadays being developed: many-body perturbation theory, Non-Equilibrium Green's Functions, Bethe-Salpeter equation, density functional theory (DFT) techniques, time-dependent DFT, first principles molecular dynamics, QM/MM, ...

The focus of this year, large sizes and complex systems, has been an opportunity to look at the limitations of the methods, both in terms of complexity of the physical phenomena and size of

the systems under study. In our opinion, the oral and poster presentations of this workshop have shown the necessity of investing effort in the continuous development of various techniques and to go beyond current limitations in the fields of:

Large-scale simulations

New developments of computational techniques that aim at large-scale simulations were presented by VandeVondele, Dubois, and Huebener. Over the last few years this field has show much progress. Tens of thousands of atoms are currently within reach. The sizes of many biological systems and active sites in organic solar cells, are however still an order of magnitude larger. Solving the computational problems that arise in these systems poses a formidable challenge. This was also clearly emphasized in lively discussion with the invited experimentalist (Medina), highlighting the problems and challenges of ab initio treatment of large biological complexes.

In order to scale to many relevant biological systems and to make use of the coming exa-scale computers more development is needed. There is however good hope that these problem will become treatable in the the near future especially by combing the different approaches discussed.

Molecular electronics

The field of molecular electronics (aka first principles electronic transport) is fast evolving, as we saw in one dedicated session. But predictive simulation of real devices is still far ahead.

Ultra-fast electron dynamics

Ultra-fast electron dynamics, and related high-intensity laser-matter interaction, is a particularly challenging problem. Some examples of the current limitations were displayed in the presentations by M. Verstraete and F. Remacle. On one hand, are the explicitly correlated time-dependent quantum chemistry approaches. These methods are slow and cumbersome, mainly because of the bad scaling of computational effort with systems size. On the other hand, the current state-of-the-art of the exchange and correlation functionals of time-dependent density-functional theory are simply not good enough for many far-from-equilibrium situations.

Many body perturbation theory

The various presentations in the field of many body perturbation theory showed that this field is constantly getting more mature. Various benchmark results are now available and the range of types of systems (solids, 1D, molecules) on which it can be used is expanding. We have seen

that - for small systems - very accurate and well defined calculations can be done. On the other hand, approximate methods to treat larger and more complex systems are being developed. We predict that the systematic benchmark of approximate methods against results obtained from high-accuracy calculations will further advance the field in the coming years.

Annex 4a: Programme of the meeting

Day	Monday 22 September
	Welcome
16:00	**ETSF SC and MB meeting**
18:00	**ETSF Software meeting**
Day	Tuesday 23 September
9:00	Registration and Opening
9:15	Electron Dynamics in Strong and Weak Fields: Studies of the Exact Correlation Potentials **N.T. Maitra**
10:05	Non-perturbative charge-transfer within TDDFT: simulations in exactly-solvable model systems **J.I. Fuks**
10:30	Coffee Break
11:10	Exact adiabatic approximation in TDDFT **J. Jokar**
11:35	On the room temperature ferroelectricity of hydrogen-bonded charge transfer crystals **G. D'Avino**
12:00	Lunch
14:00	Flavoproteins and Flavoenzymes: use of spectroscopy in the elucidation of action mechanisms **M. Medina**
14:50	Excited state structures and circularly polarized luminescence (CPL) of biologically relevant chromophores **A. Pikulska**
15:15	Tuning Far-Red Fluorescent Proteins: Insights from mPlum's Dynamic Stokes Shift **V. Moron**
15:40	Coffee Break
16:10	*Ab initio* circular dichroism and conformational flexibility of amino acids **E. Molteni**
16:35	InfraRed spectra of oxidized forms of cellulose **C. Violante**

17:30	**ETSF general meeting**
18:30	**User projects meeting**
Day	Wednesday 24 September
9:00	Many-body perturbation theory for organic photovoltaics **X. Blase**
9:50	GW Many-Body Perturbation Theory for Electron-Phonon Coupling Calculations **C. Faber**
10:15	Advancing *GW*: high throughput methods for solids and a systematic benchmark for molecules **M. van Setten**
10:40	Coffee Break
11:10	Computing the Electronic Properties of Wide Band Gap Oxides for Energy Applications: Hybrid Functional and GW Calculations **L. Caramella**
11:35	Accurate effective masses from first principles **J. Laflamme Janssen**
12:00	Lunch
14:00	Dynamical Studies of Ultrafast Charge Migration in Diatomic and Modular Molecules Probed by Photoelectron Angular Distributions **F. Remacle**
14:50	Control of electron density dynamics - comparing quantum chemistry with real time TDDFT **M. Verstraete**
15:15	Coffee Break
15:40	Correlated electron-nuclear dynamics **A. Abedi**
16:30	Incorporating static correlation effects into density functional theory **N. Helbig**
17:00	**Poster session** (with finger food)
Day	Thursday 25 September
9:00	Ultrafast dynamics of light-harvesting: insights from TDDFT **C.A. Rozzi**
9:50	Ultrafast single electron spin manipulation in 2D semiconductor quantum dots with optimally

	controlled time-dependent electric fields through spin-orbit coupling **J. Budagosky**
10:15	Coffee Break
10:45	Dynamical exchange-correlation corrections to Kohn-Sham conductances from static density functional theory **S. Kurth**
11:10	Fully optimized local orbitals for total energy, bands structure and electronic transport calculations **S. Dubois**
11:35	Transport properties of multiferroic tunnel junctions in an embedded Green-function approach **A. Neroni**
12:00	Lunch
14:00	Nonadiabatic dynamics with relativistic effects using time-dependent density functional theory **I. Tavernelli**
14:50	Ab-initio calculations of spin dependent Seebeck effect in permalloy **M. Di Gennaro**
15:15	Optical coherent current control at surfaces: theory of injection current and spin generation **B. Mendoza**
15:40	Coffee Break
16:10	The role of electron localisation in density functionals **R. Godby**
16:35	Electron-Energy Loss and Inelastic X-ray Scattering of CuO from First Principles **C. Rödl**
17:00	Hybrid atomistic/continuum model a semiconductor quantum dot coupled to metal nanoparticle: Towards a scalable and robust approach to design the optical properties of functionalised plasmonic nanostructures **M. Grüning**
19:00	Visit to Zaragoza
21:00	Social Dinner
Day	Friday 26 September
9:00	Large scale simulations with DFT: GGA and beyond **J. VandeVondele**

9:50	Efficient calculations of electronic excitations with the Sternheimer method and multishift linear system solvers **H. Hübener**
10:15	Ground state electronic structure and optical dielectric constants for solids with the *sln(s)* exchange functional **V. Vlcek**
10:40	Coffee Break
11:10	Graphene-Multiferroic heterostructures for spintronics applications **Z. Zanolli**
11:35	Exciton Dipersion in Layered Materials from First Principles **G. Fugallo**
12:00	Closing Remarks - **Rex Godby**
12:15	Lunch

Annex 4b: Full list of speakers and participants

Full list of speakers

Milagros Medina
Neepa Maitra
Ali Abedi
Joost VandeVondele
Francoise Remacle
Carlo Andrea Rozzi
Ivano Tavernelli
Xavier Blase

Victor Moron
Michiel van Setten
Jeiran Jokar
Simon Dubois
Stefan Kurth
Rex Godby
Carina Faber
Bernardo Mendoza
Anna Pikulska
Elena Molteni
Hannes Huebener
Vojtech Vlcek
Johanna I. Fuks
Jorge Budagosky
Myrta Grüning

Nicole Helbig
Jonathan Laflamme Janssen
Andrea Neroni
Zeila Zanolli
Claudia Violante
Claudia Rödl
Gabriele D'Avino
Giorgia Fugallo
Lucia Caramella
Matthieu Verstraete
Marco Di Gennaro

Full list of participants

Ali Abedi, Max-Planck-Institut für Mikrostrukturphysik
Ravikumar Abhilash, University of Milano, Bicocca
Claudio Attaccalite, Instute Neel
Xavier Blase, CNRS
Gaelle Bruant, CNRS
Jorge Budagosky, University of Zaragoza
Giancarlo Cappellini, University of Cagliari
Lucia Caramella, Dip. di Fisica - Universita' di Milano
Alberto Castro, BIFI
Sophie Chauvin, Ecole polytechnique
Andrea Cucca, LSI
Pier Luigi Cudazzo, Universidad del Pais Vasco
Gabriele D'Avino, University of Liege
Thorsten Deilmann, Instut für Festkörpertheorie
antoine Dewandre, University of Liege
Marco Di Gennaro, University of Liege
Matthias Drüppel, University of Münster
Simon Dubois, IMCN/NAPS - UCLouvain
Carina Faber, Institut Neel, CNRS
Ayman Farhat, Lebanese International University
Michael Friedrich, Universität Paderborn
Giorgia Fugallo, LSI, Ecole Polytechnique
Johanna I. Fuks, CUNY Hunter College
Tobias Förster, University of Münster
Pablo Garcia-Gonzalez, Universidad Autonoma de Madrid
Matteo Gatti, LSI Ecole Polytechnique Palaiseau
Matteo Gerosa, Politecnico di Milano
Christine Giorgetti, LSI-Ecole Polytechnique-CNRS
Rex Godby, University of York
Xavier Gonze, Universite Catholique de Louvain
Eberhard Gross, MPI of Microstructure Physics
Myrta Grüning, Queen's University Belfast
Nicole Helbig, Forschungszentrum Jülich
Hannes Huebener, University of Oxford
Jeiran Jokar, Forschungszentrum Jülich
Ksenia Komarova, Photochemistry Center
Maximilian Kulke, Universität Paderborn

Stefan Kurth, Univ. del Pais Vasco and IKERBASQUE
Jonathan Laflamme Janssen, Universite catholique de Louvain
He Lin, DIPARTIMENTO DI SCIENZA DEI MATERIALI
Mathias Ljungberg, DIPC, San Sebastian
Neepa Maitra, Hunter College CUNY New York
Federico Marchesin, CFM - DIPC
Milagros Medina, Universidad de Zaragoza
Bernardo Mendoza, Centro de Investigaciones en Optica
Elena Molteni, Universita' degli Studi di Milano
Victor Moron, EHU/UPV
Adriano Mosca Conte, University of Rome Tor Vergata
Andrea Neroni, Forschungszentrum Jülich
Valerio Olevano, Institut Neel
Micael Oliveira, University of Liege
Giovanni Onida, University of Milan - Physics Department
Anna Pikulska, University of Warsaw
Yann Pouillon, Universidad del Pais Vasco UPV/EHU
Sriram Poyyapakkam Ramkumar, Universite Catholique de Louvain
Lucie Prussel, Laboratoire des Solides Irradis
Olivia Pulci, University of Rome Tor Vergata
Lucia Reining, ETSF/CNRS
Francoise Remacle, University of Liege
Igor Reshetnyak, LSE, Ecole Polytechnique
Gian-Marco Rignanese, Universite catholique de Louvain
Pina Romaniello, Universite Toulouse III
Tuomas Rossi, Aalto University
Carlo Andrea Rozzi, CNR-NANO Modena
Doris Ruiz, University of Concepcion
Claudia Rödl, Ecole Polytechnique
Arno Schindlmayr, Universität Paderborn
Francesco Sottile, Ecole Polytechnique
Martin Stankovski, Lund University
Nicolas Tancogne-Dejean, Ecole Polytechnique
Walter Tarantino, LSI, Ecole Polytechnique, Palaiseau
Ivano Tavernelli, EPFL
Marilena Tzavala, Ecole polytechnique
Joost VandeVondele, ETH Zürich
Valerie Veniard, LSI Ecole Polytechnique CNRS
Matthieu Verstraete, University of Liege
Claudia Violante, University of Rome Tor Vergata
Vojtech Vlcek, University of Bayreuth
Marius Wanko, EHU/UPV San Sebastian
Hans-Christian Weissker, CINaM-CNRS Marseille
Jianqiang ZHOU, ETSF-Palaiseau
Zeila Zanolli, Forschungszentrum Jülich
Michiel van Setten, Universite Catholique de Louvain
Claudio Verdozzi, Lund University