TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS

5th International Workshop and School

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Summary

The fifth School and Workshop on Time-Dependent Density Functional Theory was hosted, as the previous ones, by the Benasque Center for Science. It is the fifth of a very successful series that started in 2004. The purpose has always been to (1) make a very intense introduction to both the theory, the practice, and the numerical implementation of time-dependent density-functional theory (TDDFT) mainly (but not exclusively) oriented to young scientists willing to initiate or strengthen their knowledge and skills on TDDFT, followed by (2) a workshop on the subject in which all the main aspects are to be covered by the leading experts. The physical conditions offered by the new Benasque Center for Science (http://www.benasque.org/) allow for a very fruitful and informal contact between the students and the teachers, that we strongly encouraged.

The results has been a very fruitful School, and an exciting Workshop. Regarding the School, all the pedagogical documents of the school are made available to the everybody through the webpage of the meeting (http://www.benasque.org/2012tddft/). Also, we provided all the students with the new book "Fundamanetals of Time-Dependent Density-Functional Theory", edited by M.A.L. Marques, N. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio, *Lecture Notes in Physics* **837** (Springer, Berlin/Heidelberg, 2012), as it has all the basic material to be discussed in the lectures. The students could access, throgh the lectures and the discussion with the teachers, to all the relevant aspects of the theory, as well as to the key aspects of the experimental results addressed by the theory (some experimental lecturers were invited).

Regarding the Workshop, the selection os speakers addressed the numerous open topics existing in the field. In the last part of this report, the full programme of the workshop is included.

Finally, in order to allow for the students to better discuss their research projects among themselves and with the teachers of the school, we asked them to present posters describing their current work and/or planned research project. Two of these posters were then selected as oral contributions to the international workshop and were granted the "Pedro Pascual Prize" for the best posters of the school. As in previous editions of this event, the number of applications surpassed all expectations and, of course, also the limit of places that we had to satisfy in order for the students to get the maximum benefit from the school, and also due to space and computer resource limitations.

Description of Scientific content

Since TDDFT is a rapidly evolving field of Science, the precise content of both school and workshop have changed over the years although the format of the events has been largely unaltered.

School

The School covered the topics that we believe constitute the core of the theory, and also included a few lectures about the experimental aspects that TDDFT intends to describe.

- Foundations of the theory, cornerstone theorems.
- Foundations of many-electron theory, which permits to study complementary theories for the description of many-electron dynamics: GW, Bethe-Salpether.
- Overview of spectroscopies: description of experiments, by leading experimentalists in the field.
- TDDFT approach to quantum electronic transport.
- Advanced concepts: memory, etc.
- Applications.

The theoretical work was complemented, in the afternoons, by practice work in the computer room of the Benasque Center for Science, where the students could access state-of-the-art software for TDDFT calculations. The practical work was divided in three sections:

- Software development: guided construction of a TDDFT code. The students had the opportunity of analyizing a basic TDDFT code, in order to develop skills in software engineering of this kind of programs.
- Tutorial on the `octopus` code.
- Tutorial on the `yambo` code.

Workshop

The aim of the Workshop was to assess the present status of TDDFT approaches to the study of spectroscopic properties of real materials, and explore their capability for applications in further systems with technological and biological interest. The recent developments of TDDFT covered during the workshop include TDDFT versus current-DFT, van der Waals interactions, applications to biological systems, new functionals, transport phenomena, optical spectra of solids, etc. Due to the different methods used to tackle this problem (Many-Body Theory, Density Functional Theory, Configuration Interaction, semi-empirical approaches), this Workshop was intended as a way to promote links among scientists coming from different communities

working or interested in electron excited states. Also it was intended as a follow-up event for the students attending the school as it was a good opportunity for them to see the real implications of the school lectures and get the new theoretical advances in the the development of exchange-correlation functionals as well as applications to complex systems (nanostructures, bio-molecules, interstellar molecular analysis, solids, etc.) Our goal was to bring together scientists working on foundations and different applications of TDDFT and many-body theory, trying to assess the capability of current approximations to be applied to real systems of increasing complexity. The invited and contributed talks covered:

- Fundamental topics on TDDFT, essential theorems.
- Many-Body Theory, and electron transport theory.
- New approximations to the exchange and correlation potential and kernel.
- Quantum optimal control.
- New experimental results, mainly in the areas of high intensity fields and atto-second Science.

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

The detailed program of both School and Workshop is given at the end of this document.

Two poster sessions were scheduled; the posters were hanged at the beginning of the event, and were kept at all times, so that students and participants could discuss at any time. All the posters were photographed and can be consulted at:

http://www.benasque.org/2012tddft/cgi-bin/pictures.pl

In order to incentivate the creation of good posters, we organized a contest in which the two best posters (as qualified by a poll in which all School teachers could vote) got the "Pedro Pascual Prize". These two awards were given to Federica Agostini ("Exact factorization of the time-dependent electron-nuclear wave-function: A mixed quantum-classical study", and Daniel Whitenack ("Derivative discontinuities, orbital energies and lifetimes in density functional resonance theory"). Both of them, who received equal number of votes, were invited to present their work at the Workshop.

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

The previous successes of this event is proved every time by the application numbers: In all occasions there has been a very large number of applicants for the school, that has increased every edition to become more than 100. This is not only a testimony of the strong pulse of the scientific field itself, but also of the good quality of the school. Since we want to maximize the learning experience of the students via a close interaction with the teachers (and also due to the logistic limitations imposed by the hands-on tutorial), the participants of the school have never exceeded 50. It is worth mentioning that participants came from all over the world, making this series of schools and workshops a truly global event.

The work presented at the Workshop has demonstrated the outstanding capabilities of TDDFT to describe the various forms of spectroscopy that probe the electron dynamics of matter. Spectroscopies, in general, are the tools used to study the microscopic structure of matter. The experimental results obtained with these tools can only be interpreted correctly with the help of accurate theoretical methods, capable of simulating the microscopic behavior of matter subject to external perturbations. A number of spectroscopic methods address electronic excited states (e.g. optical absorption spectroscopy, photo-electron emission spectroscopy, etc), and hence the need of first principles theoretical methods capable of addressing the excited state many-electron problem. Time-dependent density-functional theory (TDDFT) is one of such methods.

It is not, however, the only approach to the excitations of many-electron systems. In fact, more accurate (yet more expensive) techniques (based on many-body perturbation theory, for example) exist, and therefore these alternatives have also been covered in both the workshop and the school in particular their relation and comparison to TDDFT. However, TDDFT achieves a good balance between accuracy and computational cost. This workshop has clearly shown how its use is increasing, and it is fast becoming one of the tools of choice to get accurate and reliable predictions for excited-state properties in solid state physics, chemistry and biophysics, both in the linear and non-linear regimes.

We have witnessed in this Workshop the most recent developments of TDDFT (and time-dependent current functional theory): the description of photo-absorption cross section of molecules and nanostructures, electron-ion dynamics in the excited state triggered by either a small or high intense laser fields, van der Waals interactions, development of new functionals coping with memory and non-locality effects, applications to biological systems (chromophores), transport phenomena, optical spectra of solids and low- dimensional structures (as nanotubes, polymers, surfaces...).

The scientists that approach the TDDFT field face difficulties in grasping its many aspects, and we feel that for those attending the School, these difficulties have been alleviated. We believe that the School has been extremely helpful for young graduate students, post-docs that are envisaging a project for which TDDFT/MBT is the tool of choice. The event is especially useful, since we feel that the most efficient scheme for training young researchers in these techniques is to have a school where the basic theory is taught, followed by a workshop that introduces them to the forefront research in the field. The school had an equal share

of theoretical and practical classes. This eases the learning of the techniques and provides the students with the practical knowledge of the numerical aspects and difficulties, at the same time introducing them to well-established open source numerical codes. At the end of the School, the students have reached sufficient working knowledge to pursue their projects at their home institution.

During the school we have incentivated a close and informal contact between the students and the teachers. Furthermore, the students had the opportunity of talking about their current research activities and future interests. We feel that this is an important point, since young scientists should be involved in the building up of a strong community.

Finally, we mention that, as in other editions of this event, we made a survey among all participants in order to assess the level of satisfaction. We can report that in general we received a very positive feedback. Most participants found both Workshop and School to be most stimulating, even more than in past editions.

Final programme

School

Wednesday, January 4th

- 0920 0930 Opening Remarks
- 0930 1030 TDDFT I (E. K. U. Gross).
- 1030 1130 TDDFT II (E. K. U. Gross).
- 1130 1230 Introduction to Green's function (S. Kurth).
- 1230 1330 Many-Body: GW I (M. Gatti).
- 1530 1830 Introduction to the practical classes and codes.
  - Introduction to octopus (D. Strubbe).
  - Introduction to yambo (D. Sangalli).
  - Introduction to the coding exerciese (A. Castro).

Thursday, January 5th

- 0930 1030 Overview of spectroscopies I (F. Lepine).
- 1030 1130 Overview of spectroscopies II (F. Lepine).
- 1130 1230 TDDFT III (E. K. U. Gross).
- 1230 1330 Many-Body: GW II (M. Gatti).
- 1530 1830 Basic TDDFT code I.

Friday, January 6th

- 1600 1700 TDDFT IV (E. K. U. Gross).
- 1700 1800 The link between experiment and theory (S. Botti).
- 1800 1900 Many-Body: BSE I (I. Tokatly).
- 1900 2000 Many-Body: BSE II (I. Tokatly).

Saturday, January 7th

- 0930 1030 TDDFT as a tool in chemistry I (I. Tavernelli).
- 1030 1130 Models in time-dependent phenomena I (M. Lein).
- 1130 1230 Quantum transport (S. Kurth).

- 1230 1330 TDDFT as a tool in chemistry (I. Tavernelli).
- 1530 1830 Basic TDDFT code II.

Sunday, January 8th

- 1630 1730 Basic TDDFT code III.

Monday, January 9th

- 0930 1030 Advanced TDDFT I (N. Maitra).
- 1030 1130 Models for time-dependent phenomena II (M. Lein).
- 1130 1230 Advanced TDDFT II (N. Maitra).
- 1230 1330 Current TDDFT I (C. Ullrich).
- 1530 1830 octopus I.
- 1830 2000 POSTER SESSION.

Tuesday, January 10th

- 0930 1030 TDDFT as a tool in chemistry III (I. Tavernelli).
- 1030 1130 Non-linear material response properties with TDDFT (D. Strubbe).
- 1130 1230 Current TDDFT II (C. Ullrich).
- 1230 1330 Models for time-dependent phenomena III (M. Lein).
- 1530 1830 octopus II.

Wednesday, January 11th

- 0930 1030 TDDFT vs. Many-Body I (R. van Leeuwen).
- 1030 1130 TDDFT as a tool in chemistry IV (I. Tavernelli).
- 1130 1230 Overview of spectroscopies III (S. Huotari).
- 1230 1330 Advanced TDDFT III (N. Maitra).
- 1530 1830 yambo I.
- 1830 2000 POSTER SESSION.

Thursday, January 12th

- 0930 1030 TDDFT vs. Many-Body II (R. van Leeuwen).

- 1030 1130 Models for time-dependent phenomena IV (M. Lein).
- 1130 1230 Overview of spectroscopies IV (S. Huotari).
- 1230 1330 Current TDDFT III (C. Ullrich).
- 1530 1830 yambo II.
- 1830 1900 Final remarks.

Workshop

Friday, January 13th

Chairperson: C. Ullrich

- 0920 0930 Opening remarks (A. Rubio).
- 0930 1015 Time-dependent current density functional theory: Rigorous lattice formulation (I. Tokatly).
- 1010 1050 Semiclassical Correlation in Density-Matrix Propagation (N. Maitra).
- 1050 1130 Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function (A. Abedi).
- 1130 1200 COFFEE BREAK.

Chairperson: I. Tokatly

- 1200 1240 (TD)DFT: fundamentals and a new functional (M. Ruggenthaler).
- 1240 1320 Accurate density-functional methods based on correlation energy functionals within the exact- exchange random phase approximation (A. Görling).
- 1320 1400 Optics of semiconductors from meta-GGA-based time-dependent density-functional theory (V. Nazarov).

Chairperon: E. K. U. Gross.

- 1600 1640 The derivative discontinuity in transport (S. Kurth).
- 1640 1720 Electron-ion entanglement and decoherence dynamics in trans-polyacetylene oligomers (H. Appel)
- 1720 1750 COFFEE BREAK
- 1750 1830 Intersubband spin plasmons in quantum wells: spin-orbit coupling and many-body effects (C. Ullrich).

- 1830 1910 Excitation gaps of finite-sized systems from Optimally-Tuned Range-Separated Hybrid Functionals (L. Kronik).

Friday, January 13th

Chairperson: A. Castro.

- 1600 1640 How to get what you want from optimal control (C. Koch).
- 1640 1720 Optimal control of many-electron systems and quantum revival (E. Räsänen).
- 1720 1800 Show me the light: Optimal Control with Strong Lasers (D. Kammerlander).
- 1800 1830 COFFEE BREAK

Chairperson: A. Rubio.

- 1830 1910 Attosecond time-resolved molecular dynamics (M. Vrakking).
- 1910 1950 Multichannel Tunneling in Strong Field Ionization (O. Smirnova).
- 1950 2030 Probing electron excitations with inelastic x-ray scattering spectroscopies (S. Huotari).

Sunday, January 15th

Chairperson: R. van Leeuwen.

- 0930 1010 Ab initio colors (and a few thoughts on functionals for spectroscopy) (S. Baroni).
- 1010 1050 Interaction effects in time-dependent quantum transport: TDDFT versus MBPT (G. Stefanucci).
- 1050 1130 TDDFT for Electron-Phonon Dynamics with Applications to Quantum Dots (O. Prezhdo).
- 1130 1200 COFFEE BREAK

Chairperson: F. Nogueira.

- 1200 1240 Nonadiabatic molecular dynamics coupled to time dependent external potentials: towards TDDFT-based local control (I. Tavernelli).
- 1240 1320 Progress at the interface of wave function and density functional theories (N. Gidopoulos).

Chairperson: S. Kurth

- 1530 1610 Towards inclusion of dissipation in TDDFT (E. Suraud).

- 1610 1650 Beyond the Hubbard model: a realistic description of metal-insulator transitions in transition-metal oxides (M. Gatti).
- 1650 1730 Plasmonics and non-local interactions from TDDFT: graphene and metal surfaces (T. Olsen).
- 1730 1750 COFFEE BREAK.
- 1750 1830 Photoinduced charge separation in light-harvesting supramolecular systems (C. A. Rozzi).
- 1830 1850 Exact factorization of the time-dependent electron-nuclear wave-function: A mixed quantum- classical studio (F. Agostini, poster prize award).
- 1850 1910 Derivative Discontinuities, Orbital Energies and Lifetimes in Density Functional Resonance Theory (D. Whitenack, poster prize award).

Monday, January 16th

Chairperson: N. Maitra

- 0900 0940 The interaction of ultrashort high-intensity x-ray pulses with dense atomic gases (N. Rohringer).
- 0940 1020 Studies of dipole-forbidden electronic excitations (A. Sakko).
- 1020 1050 COFFEE BREAK.
- 1130 1210 Bootstrap approximation for exchange-correlation kernel of TD-DFT (S. Sharma).
- 1130 1210 Role of discontinuities in linear response TDDFT (M. Hellgren).
- 1210 1220 FINAL REMARKS.