Preface

Back in 2004 while celebrating the twentieth anniversary of the discovery of time-dependent density functional theory (TDDFT) we decided to take on the endeavor of making TDDFT really accessible to all students and researchers. Although a relatively young field, TDDFT was already beginning to rise as a method of choice in Materials Science and Quantum Chemistry, for the description of spectroscopic and non-equilibrium properties of both finite and extended systems. To this end, we set up the Benasque TDDFT series of school and workshops, a 2 week intensive meeting on TDDFT held every 2 years, nested in the beautiful Pyrenees. The Benasque TDDFT meeting is now well-established as the key training event and conference in the field. Now that we are facing the fifth edition of the event, we felt it was timely to have a pedagogical edition of our original 2006 book on TDDFT. The present volume is not a re-edition but a real new project that shares a few parts with the old book, but that has far more focus on the fundamentals and also includes new developments of the last few years of this rapidly-evolving field. Thus we give it the title of "Fundamentals of Time-Dependent Density Functional Theory".

A Little History

The first International School and Workshop on Time-Dependent Density Functional Theory was hosted by the Benasque Center for Science, Spain from August 28th to September 12th, 2004. The aim of the School was to introduce theoretical, practical, and numerical aspects of TDDFT to young graduate students, post-docs and even older scientists who were envisaging a project for which TDDFT would be the tool of choice. The School has 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, while at the same time introducing them to well-established open source numerical codes (e.g., OCTOPUS, http://www.tddft.org/programs/octopus). The School is followed by a

Workshop where talks are presented by leading scientists on their current research, with a schedule designed for plenty of informal discussion. This introduces the students to the forefront of TDDFT research and rounds out their training well. At the end the participants should have sufficient working knowledge to pursue their projects at their home institution. The outstanding success of the first School led to the organization of another four events, held again in Benasque, from August 27th to September 11th 2006; August 31st to September 15th 2008, January 2nd to 15th 2010, and January 4th to 17th 2012. Simultaneously, a similar sequence of events happened on the other side of the Atlantic: From June 5–10 2004, a Summer School on TDDFT was held in Santa Fe, USA. This event sparked the establishment of a series of Gordon Research Conferences on TDDFT which began in 2007.

A very tangible outcome of the two events in 2004 was the publication of a Springer Lecture Notes book, [*Time-Dependent Density-Functional Theory* edited by M. A. L. Marques, C. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, vol. 706 of *Lecture Notes in Physics* (Springer Verlag, Berlin, 2006)]. This consists of contributions from speakers at the first Benasque School and Workshop in 2004 as well as contributions from the Summer School in Santa Fe. The book was the first comprehensive review of the field. It is now on the bookshelf of many scientists and, perhaps more importantly, has been used by hundreds of students and postdocs to enter the field of TDDFT. It was also the main reference used in the later Benasque TDDFT Schools, helping over 250 students to be introduced to the theory and its applications. However, TDDFT is a fast evolving field, and much progress has been achieved in the past 5 years, which motivated us to consider compiling a revised edition. After extensive discussions among ourselves, with other scientists, and with many students of the last Benasque school, a set of recommendations emerged, both for the book as a whole, and also for the individual chapters. We concluded that we could take this opportunity not only to update the book, but also to refocus it to be more coherent, fundamental, and pedagogical (for the students), as well as to sometimes provide a different perspective on TDDFT. The result is the current volume you hold in your hands. We hope you will enjoy and learn from it as much as we have enjoyed and learned from putting it together.

A User's Guide

Time-dependent density-functional theory is a rigorous reformulation of the non-relativistic time-dependent quantum mechanics of many-body systems that places the time-dependent one-body density of a many-body interacting system at center stage. It is an extension of ground-state density functional theory, to which it is similar in philosophy, but its formulation and functionals are very different, and contain different physics. Today, the use of TDDFT is increasing in all areas where interactions are important but the direct solution of the Schrödinger equation is too

demanding. Indeed, we have witnessed exponential growth of the number of articles published in this field, not unlike what occurred in ground-state density functional theory twenty years ago. High-level scientific meetings focusing on TDDFT have materialized; notably, aside from the Benasque School and Workshop, the Gordon Research Conferences in TDDFT, focused sessions and pre-meeting tutorials on TDDFT at the American Physical Society and American Chemical Society meetings, and CECAM workshops.

Despite tremendous effort focused over the years, a first-principles theoretical and practical description of the interaction of molecules with time-dependent electromagnetic fields is still a challenging problem. In fact, we are still lacking a definitive and systematic methodology, capable of bridging the different spatial and time scales that are relevant for the description of light-induced processes in nanostructures, biomolecules and extended systems with predictive power. Due to its unparalleled balance between the computational load that it requires and the accuracy that it provides, TDDFT has repeatedly shown its usefulness in the last decade when attempting this challenge. TDDFT is now a tool of choice to get quite accurate and reliable predictions for excited-state properties in solid state physics, chemistry and biophysics, both in the linear and non-linear regimes. It is routinely used for the description of photo-absorption cross section of molecules and nanostructures, electron-ion dynamics in the excited state triggered by either weak or intense laser fields, van der Waals interactions, applications to biological systems (chromophores), transport phenomena, optical spectra of solids and low-dimensional structures (such as nanotubes, polymers, surfaces, et cetera).

At the same time, however, there are important cases for which the functional approximations in use today perform poorly. One of the major on-going challenges is in the development of approximations of improved accuracy especially for phenomena important in applications of urgent interest today, such as charge-transfer processes and photo-dynamics in solar cell devices. To develop accurate and reliable approximations, a solid understanding and appreciation of the fundamental theory, as well as recent developments in theory and applications, is required. We hope this book will be useful in this regard.

In this book we focus largely on the fundamentals of the theory, but also in setting direct links with the different experimental observables and tools. We introduce all the basic concepts and build up in complexity all the way to the open problems we are facing nowadays. This book is divided into six parts. Part I presents an overview of the experimental spectroscopic techniques in use today and puts in context the need for a theoretical framework capable of describing the non-equilibrium dynamics of complex systems at different time and length scales. Part II addresses all the basic theory and fundamentals of TDDFT. More advanced concepts related to the construction of exchange-correlation functionals including dispersion forces and open quantum systems are addressed in part III. The next part addresses the realm of real-time TDDFT, namely the simulation in real-time of the combined electron-ion dynamics of real systems, from non-equilibrium excited state dynamics to molecular transport. Numerical details of the implementation of the theory discussed in the earlier sections are addressed in detail in

part V, including new developments for massive parallel architectures and graphic processing units (GPUs). Part VI places TDDFT in comparison with other related theoretical frameworks developed over the years to address similar phenomena.

The Editors

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