Preface

Density-functional theory (DFT) is an enormously appealing method for determining the microscopic properties of matter. In quantum mechanics, the basic procedure is to start from Schrödinger's equation for the system of interest, be it an atom, a molecule, or a solid, and find the desired observables from the wave function. This is conceptually straightforward but becomes tedious as soon as there are more than just a few electrons. DFT instead proposes something radically different: forget about wave functions—the ground-state particle density, as shown by Hohenberg and Kohn in 1964, contains in principle enough information to determine all we need to know about any system. And it gets better: according to Kohn and Sham (1965), the density can be determined relatively easily by solving an effective one-particle problem!

But there is a price to be paid. The intricacies of the many-body problem are hidden away in the so-called exchange–correlation energy, which is a functional of the density (hence the name DFT). We don't know its exact form; approximations are unavoidable. Fortunately, the past decades have witnessed a steady stream of better and better exchange–correlation functionals, leading to more and more accurate results at low computational cost. This has fostered rapid growth in the popularity of DFT in physics, chemistry, materials science, biochemistry, and many other areas.

While DFT has been extremely successful for structural properties, there are many important issues which extend beyond its reach. Most notably, time-dependent processes and excited-state properties of electronic systems either are not included at all or are not easily accessible. This has motivated the development of time-dependent density-functional theory (TDDFT).

TDDFT is of relatively recent origin, dating back to the mid 1980s. It is an even stranger theory than DFT: the core idea is that the dynamics of any system of interacting fermions is completely encoded in its time-dependent density, which renders the wave function unnecessary. Again, the density can in principle be calculated relatively easily, but to do so, we need to deal with exchange–correlation effects that are even more involved than in the static case. In view of this, it almost borders on a miracle that we can actually find approximations that produce accurate results (and if they don't, that we can understand why).

Over the past few years there has been a flurry of activity in TDDFT, in particular when it became clear that this offers a superior alternative to traditional quantum chemistry methods for calculating optical excitation spectra of large molecules. The number of scientific publications using TDDFT methods continues to grow exponentially, with new applications in areas such as photosynthesis and photovoltaics, electronic transport through single molecules, ultrafast molecular dynamics, and laser control of chemical reactions. Over the past few years there have been several conferences, workshops, and schools dedicated solely to the subject of TDDFT.

All of this is evidence that TDDFT has become well defined as a subject on its own, with a growing community of scientists that constitutes a subset of the larger DFT community, yet has its own distinct character and speaks its own jargon. This book is a reflection of these exciting developments.

The purpose of this book is to provide readers at the graduate level with the necessary information and resources so they can learn TDDFT. But what does this mean? And what does one have to learn? That, of course, depends on one's particular needs. Everyday users of computer codes in quantum chemistry or materials science may encounter (TD)DFT only through menu options for the exchange–correlation functional. But it can take considerable experience to make a good choice: one needs to know how the various functionals perform compared with one another, and how to avoid potential pitfalls. Such experience is best gained by studying instructive examples. On the other hand, there is a smaller but very vibrant community of developers of TDDFT methodologies. For them, formal considerations, proofs, and technical details may be most important, but they should also know how the theory performs in practice.

In order to learn TDDFT, you first need to know DFT. This is a simple but somewhat loaded statement. Practically all TDDFT calculations start with a system in the ground state, which is prepared using DFT. Furthermore, many of the concepts and functionals of the time-dependent theory have been adapted from their static counterparts. This book therefore begins with an extensive and self-contained review of DFT.

However, it needs to be emphasized that TDDFT itself is much more than just an extension of DFT: the two theories are in fact *very different*! Just consider the existence proofs: in the time-dependent theory there is no minimum principle, and we have to worry about things like memory, causality, and initial states. On the practical level, both are highly interdisciplinary theories, with applications in physics, (bio)chemistry, materials science, and other areas. But DFT is concerned with structure, whereas TDDFT is concerned with dynamics.

Science books are often categorized either as textbooks or as monographs. The former are intended to teach the basics of a field to the newcomer. The latter are more specialized and mainly written for experts. In the end, this book has turned out to be a textbook *and* a monograph, and I hope I have succeeded in finding the right balance. I have tried to be as detailed and pedagogical as possible in the basic derivations and proofs, and to give many examples and exercises. Since TDDFT is such an interdisciplinary field, there are many special topics. They are introduced in such a way that little or no prior knowledge is required. But the book also contains over 800 references, and many additional resources in the appendices. As such, I believe that it captures the present state of the art in TDDFT.

I started this book in 2008, and have been working on it pretty much continuously over the past three years. It has grown to over 500 pages, since there was such a wealth of material to choose from—and, as every author knows, a book tends to take on a life on its own! To help readers find their way, Section 1.2 serves as a roadmap, in which I explain how the book is organized.

I have tried to do my best to cite the most relevant original references; limiting the selection was, of course, unavoidable. I apologize to all those authors whose work has

been omitted owing to an oversight of mine. Needless to say, typographical, mathematical, and other mistakes will be inevitable as well. Many of the most glaring errors and omissions were caught by colleagues and friends who were so kind as to serve as proofreaders. All the remaining mistakes are entirely my own. Corrigenda and addenda will be made available online at `http://www.missouri.edu/~ullrichc/tddft-book`.

I would like to acknowledge the hospitality of the Kavli Institute of Theoretical Physics at UC Santa Barbara, where parts of this book were written during a workshop in the fall of 2009. I also thank the University of Missouri-Columbia for granting me research leave during the 2009/2010 academic year.

There is a long list of colleagues and friends with whom I have interacted over many years, and I am deeply grateful for all their support and encouragement. In the first place, I would like to thank Neepa Maitra, Giovanni Vignale, Klaus Capelle, Stefano Pittalis, Oleg Vydrov, Robert van Leeuwen, and Suchi Guha for reading parts of the manuscript and making invaluable suggestions. I have profited from the knowledge and insight of many people in the (TD)DFT community and beyond. In particular, I wish to acknowledge many fruitful and enjoyable discussions with Kieron Burke, Filipp Furche, Troy Van Voorhis, Angel Rubio, Walter Thiel, John Rehr, Claudia Ambrosch-Draxl, André Bandrauk, Massimiliano Di Ventra, Roberto D'Agosta, Heiko Appel, Ilya Tokatly, Paul De Boeij, Lucia Reining, and Irene D'Amico.

I also want to give credit to my past and current group members Harshani Wijewardane, Yonghui Li, Daniel Vieira, Ednilsom Orestes, Fedir Kyrychenko, Volodymyr Turkowski, and Aritz Leonardo. This book is dedicated to all current and future students of TDDFT, in the hope that it will make a difference.

I feel incredibly fortunate that I was able to spend my years as a student and postdoc under the guidance and support of wonderful teachers and mentors: Hardy Gross, Paul-Gerhard Reinhard, Eric Suraud, Giovanni Vignale, Michael Flatté, and Walter Kohn. I would like to express my deepest gratitude to them.

Finally, I thank Wolfram Ullrich for the original cover art, and Sonke Adlung and the editorial staff at Oxford University Press for their constant encouragement, professional support, and patience.

And thank you, Suchi, for everything.

Columbia, May 2011