M. A. L. Marques
C. A. Ullrich
F. Nogueira
A. Rubio
K. Burke
E. K. U. Gross

(Eds.)

Time-Dependent Density Functional Theory

Miguel A.L. Marques   Carsten A. Ullrich
Fernando Nogueira   Angel Rubio
Kieron Burke   Eberhard K.U. Gross

Time-Dependent
Density Functional Theory

Springer

Editors

Miguel A.L. Marques
Departamento de Física
Universidade de Coimbra
Rua Larga 3004 – 516
Coimbra, Portugal
E-mail: marques@tddft.org

Carsten A. Ullrich
Department of Physics
University of Missouri-Columbia
Columbia, MO 65211, U.S.A.
E-mail: ullrichc@missouri.edu

Fernando Nogueira
Departamento de Física
Universidade de Coimbra
Rua Larga 3004 – 516
Coimbra, Portugal
E-mail: fnog@teor.fis.uc.pt

Angel Rubio
Dpto. Fisica de Materiales
Facultad de Quimicas, U. Pais Vasco
Centro Mixto CSIC-UPV/EHU, DIPC
Apdo. 1072, 20018 San Sebastian, Spain
E-mail: arubio@sc.ehu.es

Kieron Burke
Dept. of Chemistry & Chem. Biology
Rutgers University
610 Taylor Rd, Piscataway
NJ 08854, U.S.A.
E-mail: kieron@dft.rutgers.edu

Eberhard K. U. Gross
Institut für Theoretische Physik
Freie Universität Berlin
Arnimallee 14
14195 Berlin, Germany
E-mail: hardy@physik.fu-berlin.de

Lecture Notes in Physics

The Lecture Notes in Physics

The series Lecture Notes in Physics (LNP), founded in 1969, reports new developments in physics research and teaching – quickly and informally, but with a high quality and the explicit aim to summarize and communicate current knowledge in an accessible way. Books published in this series are conceived as bridging material between advanced graduate textbooks and the forefront of research to serve the following purposes:

● to be a compact and modern up-to-date source of reference on a well-defined topic;

● to serve as an accessible introduction to the field to postgraduate students and nonspecialist researchers from related areas;

● to be a source of advanced teaching material for specialized seminars, courses and schools.

Both monographs and multi-author volumes will be considered for publication. Edited volumes should, however, consist of a very limited number of contributions only. Proceedings will not be considered for LNP.

Volumes published in LNP are disseminated both in print and in electronic formats, the electronic archive is available at springerlink.com. The series content is indexed, abstracted and referenced by many abstracting and information services, bibliographic networks, subscription agencies, library networks, and consortia.

Proposals should be sent to a member of the Editorial Board, or directly to the managing editor at Springer:

Preface

The year 2004 was a remarkable one for the growing field of time-dependent density functional theory (TDDFT). Not only did we celebrate the 40th anniversary of the Hohenberg-Kohn paper, which had laid the foundation for ground-state density functional theory (DFT), but it was also the 20th anniversary of the work by Runge and Gross, establishing a firm footing for the time-dependent theory. Because the field has grown to such prominence, and has spread to so many areas of science (from materials to biochemistry), we feel that a volume dedicated to TDDFT is most timely.

TDDFT is based on a set of ideas and theorems quite distinct from those governing ground-state DFT, but employing similar techniques. It is far more than just applying ground-state DFT to time-dependent problems, as it involves its own exact theorems and new and different density functionals. Presently, the most popular application is the extraction of electronic excited-state properties, especially transition frequencies. By applying TDDFT after the ground state of a molecule has been found, we can explore and understand the complexity of its spectrum, thus providing much more information about the species. TDDFT has a especially strong impact in the photochemistry of biological molecules, where the molecules are too large to be handled by traditional quantum chemical methods, and are too complex to be understood with simple empirical frontier orbital theory.

Today, the use of TDDFT is continuously growing in all areas where interactions are important, but direct solution of the Schrödinger equation is too demanding. New and exciting applications are beginning to emerge, from ground-state energies extracted from TDDFT to transport through single molecules, to high-intensity laser and nonequilibrium phenomena, to nonadiabatic excited-state dynamics, to low-energy electron scattering. In each case, the present approximations were applied, and found to work well for some properties, but occasionally fail for others. Thus the search for more accurate, reliable approximations will continue, and over time, should attain the same maturity as present ground-state DFT.

So, whether you're a physicist calculating optical absorption of a metal cluster, or a chemist trying to determine the HOMO and LUMO for a chromophore, we hope you'll try TDDFT, and be pleasantly surprised at the usefulness of the results. And may the force (or at least, a good functional) be with you.

The Editors

User's Guide

This book is not the usual compendium of independent research articles that results from having many contributors. We, the editors, share a common aim of providing an accessible introduction to the subject, a comprehesive review of today's applications of TDDFT, and a survey of some of the most recent work. We have worked hard to do this, and so have the many contributors. Among many other things, there is a common notation and set of abbreviations (see front pages) and a single, comprehensive set of references (see index).

We hope this volume will be useful to a variety of audiences, who can use the book in many different ways. We imagine the following:

Students. In editing this book, we assumed a basic familiarity with the concepts and applications of ground-state DFT. For the student wholly new to DFT, we strongly recommend the book, *A Primer in DFT* [Fiolhais 2003], as background reading *before* this one.

Experienced Users of Ground-State DFT. For these researchers, we hope this book shows how TDDFT goes beyond the ground state, and provides both the conceptual framework and many examples of applications and implementations.

Users of TDDFT. The book provides the conceptual underpinnings of the formal theory and a survery of implementations and applications. For example, those solving the Casida linear response equations might be interested in the various real-time methodologies, and vice versa.

Developers of TDDFT. The book shows the broad scope of present-day applications, and gives a reference for many of the developments up to the current time, and also includes novel applications.

This volume is composed of a general introduction to TDDFT (Basics), followed by 32 refereed contributions divided in six parts. In the following we give a brief overview of these contributions and try to place them in a more general context.

Basics. The first chapter is a brief introduction to the entire subject of TDDFT, and should really be read by anyone using this book. It is simple

and straightforward and explains how TDDFT works, including the original proof of Runge and Gross.

Formal Theory. The first part of the book deals with formal theory. This is a collection of chapters on general topics within TDDFT, either fleshing out some of the more esoteric consequences of the theory or generalizing it in some way or another. We start by adding to the original theorem, especially discussing the action functional and the Keldysh formalism as a very natural and useful description of the exact quantum mechanics of many-body systems under time-dependent perturbations, which can then be related to TDDFT. Next the difficult problem of initial-state dependence and its relation to memory in TDDFT is addressed. We then provide the motivation behind sometimes preferring time-dependent current DFT to TDDFT in Chap. 5. There are several cases throughout the book, e.g., for the description of transport or for the calculation of optical response of solids, where this change of variables makes for better approximations. Then we move to Chap. 6, where the first steps towards a theory including both nuclei and electrons on the same footing are given, which is extremely important for, e.g., photodissociation. We conclude this section with Chap. 7, which applies the language of second harmonic response, including super-operators and generalized response functions, to TDDFT.

Approximate Functionals. The heart of every practical DFT treatment of matter is the approximation for the xc functionals. As the theory is exact in principle, the quality of the results depends on the quality of the functional used.

Any ground-state functional yields an adiabatic approximation for use in TDDFT, and most calculations today are performed with such functionals. But many groups are searching for approximations that go beyond this, i.e., functionals with memory. In this context, we show a geometric approach based on ALDA that produces the time-dependent deformation approximation. Then, from a completely different starting point, we consider orbital-dependent functionals, and so we begin with exact exchange and then move to non-universal functional approximations to the kernel based on a correspondence with many-body perturbation theory. Lastly, Chap. 11 reviews the exact conditions of DFT and TDDFT, which should prove useful in guiding construction of approximations or testing them.

Numerical Aspects. For anyone considering performing a TDDFT calculation, there is always the choice of the numerical implementation. For strong fields, one needs to solve the time-dependent Schrödinger equation in real time. If only the optical response is needed, one can choose between real time or frequency space. This is ontop of the choice of basis sets, which can be loosely divided into real-space grids, localized basis functions, or planewaves for periodic codes. Chapter 12 surveys real-time methods for the time-dependent Schrödinger equation, and what happens when they are applied to the time-

dependent Kohn-Sham equations. Then we present the intricacies of the linear response formalism in a basis set, and in Chap. 14 we discuss molecular dynamics in a TDDFT excited state. We end this Part with a comparison of time- versus frequency-space techniques.

Applications: Linear Response. This is our largest part, demonstrating the huge variety of systems that linear response TDDFT has been applied to. The highly interesting and particularly difficult case of open-shell molecules is discussed in Chap. 16. There have been many applications to clusters, as described in Chap. 17, and to semiconductor nanostructures, using current density functionals, as discussed in Chap. 18. Progress for extended systems has been more challenging, as local and semilocal density functionals fail in the thermodynamic limit (although current-density and orbital functionals do not). This general feature is discussed in Chapters 19 and 20. This basic difficulty also appears in the polarizability of conjugated polymers, and it is analysed in the following chapter.

The bulk of the applications so far have been to molecules, especially those of biological significance. Chapter 22 discuss in detail how TDDFT can be combined with biochemical methods to extract information on biological chromophores, while Chap. 23 gives a broad survey of these applications.

Applications: Beyond Linear Response. Another area where TDDFT promises to have major impact is in the rapidly-growing field of atoms and molecules in strong laser fields. With the advent of attosecond pulses, there is great demand for efficient methods of solution of the full time-dependent Schrödinger equation. An overview is given in the opening chapter. While some impressive progress has been made here, difficulties abound, such as the calculation of multiple ionization probabilities. Non-linear phenomena in clusters are discussed in Chap. 26. This part closes with a chapter on excited-state dynamics in solids.

New Frontiers. The last part of this volume deals with some recent novel applications of TDDFT. The first three chapters discuss how to use linear-response TDDFT to tackle problems that are difficult for ground-state DFT. For example, these include correct dissociation of molecules, and the inclusion of van der Waals forces between fragments of matter. These ideas are first tested in the simplest possible case, the uniform gas in Chap. 28. Then Chap. 29 shows how to find the exchange-correlation potential from such calculations, and how it leads to improved band-gaps for solids. Finally, Chap. 30 provides a detailed survey of how this formalism produces van der Waals interactions and results for weakly interacting slabs.

The next two chapters deal with the modern problem of how to calculate the transport characteristics of an atomic-sized transistor, such as a single molecule. Two different formalisms are presented, both going beyond the treatment common in present-day calculations. The first one starts from a Master equation for the electrons coupled to the phonons, instead of the

pure time-dependent Schrödinger equation. The second one uses the Keldysh formalism described in Chap. 3 to produce a purely (time-dependent) electronic approach to the problem.

Our ultimate chapter focusses on a problem that Gross had in mind when formulating modern TDDFT, namely that of scattering. Linear-response TD-DFT is shown to yield information on continuum states as well as bound ones, including elastic scattering of electrons from atoms and molecules.

We expect that these and other new developments will bear fruit over the next several years.

List of Contributors

Carl-Olof Almbladh
Department of Solid State Theory
Institute of Physics
Lund University, Sölvegatan 14 A
S-223 62 Lund
Sweden
Carl-Olof.Almbladh@
teorfys.lu.se

André D. Bandrauk
Département de Chimie
Faculté de Sciences
Université de Sherbrooke
Sherbrooke (Québec)
Canada J1K 2R1
Andre.Bandrauk@USherbrooke.ca

Kieron Burke
Dept. of Chemistry & Chem. Biology
Rutgers University
610 Taylor Rd, Piscataway
NJ 08854, U.S.A.
kieron@dft.rutgers.edu
http://dft.rutgers.edu/

Roberto Car
Princeton University
Chemistry Physics
and Materials Institute
Washington Road, Princeton
NJ 08544, U.S.A.
rcar@Princeton.edu
http://www.princeton.edu/
~cargroup/

Mark E. Casida
Laboratoire d'Études Dynamiques
et Structurales de la Selectivité
(LÉDSS)
Institut de Chimie Moléculaire
de Grenoble
Université Joseph Fourier
(Grenoble I)
F-38041 Genoble Cedex 9, France
mark.casida@ujf-grenoble.fr

Alberto Castro
Institut für Theoretische Physik
Freie Universität Berlin
Arnimalle 14
D-14195 Berlin, Germany
alberto@physik.fu-berlin.de

James R. Chelikowsky
Institute for Computational
Engineering and Sciences (ICES)
(C0200)
ACES Building, Room 4.324
201 East 24th Street ACES
1 University Station
University of Texas at Austin
Austin, Texas 78712, U.S.A.
jrc@ices.utexas.edu
http://tesla.ices.utexas.edu/

Adam E. Cohen
Department of Physics
Stanford University
382 Via Lomita, Stanford CA 94305
U.S.A.
aecohen@stanford.edu

Felipe Cordova
Laboratoire d'Études Dynamiques
et Structurales de la Selectivité
(LÉDSS)
Institut de Chimie Moléculaire de
Grenoble
Université Joseph Fourier
(Grenoble I)
F-38041 Genoble Cedex 9, France
felipe.cordova@ujf-grenoble.fr

Nils E. Dahlen
Theoretical Chemistry
Materials Science Centre
Rijksuniversiteit Groningen
Nijenborgh 4
NL-9747 AG Groningen
The Netherlands
N.E.Dahlen@rug.nl

Paul L. de Boeij
Theoretical Chemistry
Materials Science Centre
Rijksuniversiteit Groningen
Nijenborgh 4
NL-9747 AG Groningen
The Netherlands
p.l.de.boeij@rug.nl
http://theochem.chem.rug.nl/
~deboeij

Rodolfo Del Sole
Via della Ricerca Scientifica 1
I-00133 Rome
Italy
Rodolfo.Delsole@roma2.infn.it

John Dobson
School of Science
Griffith University
Nathan Queensland 4111, Australia
j.dobson@griffith.edu.au

Martin Fuchs
Fritz-Haber-Institut der MPG
Faradayweg 4-6
D-14195 Berlin, Germany
fuchs@fhi-berlin.mpg.de

Filipp Furche
Institut für Physikalische Chemie
Lehrstuhl für Theoretische Chemie
Universität Karlsruhe (TH)
Kaiserstrasse 12
D-76128 Karlsruhe, Germany
filipp.furche@chemie.
uni-karlsruhe.de

Pablo García-González
Departamento de Física
Fundamental
Universidad Nacional de
Educación a Distancia
Apto. 60141
E-28080 Madrid
Spain
pgarcia@fisfun.uned.es

Ralph Gebauer
The Abdus Salam International
Centre for Theoretical Physics
(ICTP)
Condensed Matter Section
Strada Costiera 11
I-34014 Trieste, Italy
rgebauer@ictp.trieste.it

Andreas Görling
Lehrstuhl für Theoretische Chemie
Universität Erlangen-Nürnberg
Egerlandstr. 3
D-91058 Erlangen
Germany
Andreas.Goerling@chemie.
uni-erlangen.de

Eberhard K. U. Gross
Institut für Theoretische Physik
Freie Universität Berlin
Arnimallee 14
D-14195 Berlin
Germany
hardy@physik.fu-berlin.de
http://www.physik.fu-berlin.
de/~ag-gross/

Upendra Harbola
Department of Chemistry
University of California
Irvine, CA 92697-2025
U.S.A.
uharbola@uci.edu

Jürg Hutter
Physical Chemistry Institute
University of Zurich
Winterthurerstrasse 190
CH-8057 Zurich, Switzerland
hutter@pci.unizh.ch

Andrei Ipatov
Laboratoire d'Études Dynamiques
et Structurales de la Selectivité
(LÉDSS)
Institut de Chimie Moléculaire
de Grenoble
Université Joseph Fourier
(Grenoble I)
F-38041 Genoble Cedex 9, France
andrei.ipatov@ujf-grenoble.fr

Stefan Kurth
Institut für Theoretische Physik
Freie Universität Berlin
Arnimalle 14
D-14195 Berlin
Germany
kurth@physik.fu-berlin.de

Manfred Lein
Max-Planck-Institut für Kernphysik
Saupfercheckweg 1
D-69117 Heidelberg
Germany
manfred.lein@mpi-hd.mpg.de
http://www.mpi-hd.mpg.de/
keitel/mlein/

Xabier Lopez
Kimika Fakultatea
Euskal Herriko Unibertsitatea

E-20080 Donostia
Spain
poplopex@sq.ehu.es
http://www.sc.ehu.es/powgep99/
dcytp/teoricos/xabier/english.
html

Neepa T. Maitra
Department of Physics
and Astronomy
Hunter College and City University
of New York
695 Park Avenue, New York
NY 10021, U.S.A.
nmaitra@hunter.cuny.edu
http://www.ph.hunter.cuny.edu/
faculty/Maitra/neepa.html

Andrea Marini
Department of Physics
University of Rome "Tor Vergata"
Via della ricerca scientifica 1
I-0133 Rome, Italy
andrea.marini@roma2.infn.it
http://people.roma2.infn.it/
~marini/

Miguel A. L. Marques
Departamento de Física
Universidade de Coimbra
Rua Larga
P-3004 516 Coimbra
Portugal
marques@tddft.org

Yoshiyuki Miyamoto
Fundamental Research Laboratories
NEC Corporation
34, Miyukigaoka
Tsukuba, Ibaraki 305-8501
Japan
y-miyamoto@ce.jp.nec.com

Shaul Mukamel
Department of Chemistry
University of California
Irvine, CA 92697-2025
U.S.A.
smukamel@uci.edu
http://mukamel.ps.uci.edu

Yann M. Niquet
Atomistic Simulation Laboratory
CEA/DRFMC/SP2M/L_Sim
17 avenue des Martyrs
F-38054 Grenoble Cedex 9
France
yniquet@cea.fr

Fernando Nogueira
Departamento de Física
Universidade de Coimbra
Rua Larga
P-3004 516 Coimbra
Portugal
fnog@teor.fis.uc.pt

Dmitrij Rappoport
Institut für Physikalische Chemie
Lehrstuhl für Theoretische Chemie
Universität Karlsruhe (TH)
Kaiserstrasse 12
D-76128 Karlsruhe
Germany
rappoport@chemie.uni-karlsruhe
.de

Paul-Gerhard Reinhard
Institut für Theoretische Physik
Universität Erlangen
Staudtstr. 7
D-91058 Erlangen
Germany
reinhard@theorie2.physik.
uni-erlangen.de

Angel Rubio
Dpto. Fisica de Materiales
Facultad de Quimicas
U. Pais Vasco
Centro Mixto CSIC-UPV/EHU
DIPC Apdo. 1072
E-20018 San Sebastian
Spain
arubio@sc.ehu.es
http://dipc.ehu.es/arubio/

Yousef Saad
Department of Computer Science
and Engineering
University of Minnesota
4-192 EE/CSci Building
200 Union Street S.E. Minneapolis
MN 55455, U.S.A.
saad@cs.umn.edu
http://www-users.cs.umn.edu/
~saad/

Gianluca Stefanucci
Institut für Theoretische Physik
Freie Universität Berlin
Arnimalle 14
D-14195 Berlin
Germany
gianluca.stefanucci@
teorfys.lu.se

Osamu Sugino
Fundamental Research Laboratories
NEC Corporation
34, Miyukigaoka
Tsukuba, Ibaraki 305-8501
Japan
sugino@issp.u-tokyo.ac.jp

Eric Suraud
Laboratoire de Physique Theéorique
Université Paul Sabatier
118 Route de Narbonne
F-31062 Toulouse cedex, France
suraud@irsamc.ups-tlse.fr

Ilya V. Tokatly
Lehrstuhl für Theoretische
Festkörperphysik
Universität Erlanger
Staudtstr. 7/B2
D-91058 Erlangen
Germany
Ilya.Tokatly@physik.
uni-erlangen.de

Carsten A. Ullrich
Department of Physics
University of Missouri-Columbia
Columbia, MO 65211, U.S.A.
ullrichc@missouri.edu
http://www.missouri.edu/
~ullrichc/

Robert van Leeuwen
Theoretical Chemistry
Materials Science Centre
Rijksuniversiteit Groningen
Nijenborgh 4
NL-9747 AG Groningen
The Netherlands
R.van.Leeuwen@rug.nl
http://theochem.chem.rug.nl/
~leeuwen

Igor Vasiliev
Department of Physics
MSC 3D
New Mexico State University
P.O. Box 30001
Las Cruces, NM 88003-8001, U.S.A.
vasiliev@nmsu.edu

Valérie Véniard
Laboratoire des Solides Irradiés
CNRS-CEA-École Polytechnique
91128 Palaiseau, France
vv@ccr.jussieu.fr

Giovanni Vignale
Department of Physics
University of Missouri-Columbia
Columbia, MO 65211, U.S.A.
vignaleg@missouri.edu
http://www.missouri.
edu/~physwww/people/
GiovanniVignale.html

Ulf von Barth
Department of Solid State Theory
Institute of Physics
Lund University, Sölvegatan 14 A
S-223 62 Lund, Sweden
Ulf.von_Barth@teorfys.lu.se

Adam Wasserman
Dept. of Chemistry & Chem. Biology
Rutgers University
610 Taylor Rd, Piscataway
NJ 08854, U.S.A.
awasser@rutchem.rutgers.edu

Abbreviations

AA	Adiabatic approximation
ACFD	Adiabatic-connection and fluctuation-dissipation
ALDA	Adiabatic local density approximation (see TDLDA)
AMED	Average magitude of energy denominators
ATD	Above-threshold dissociation
ATI	Above-threshold ionization
B3LYP	Becke's three-parameter hybrid with Lee, Yang, and Parr correlation
BP86	Becke and Perdew 1986
BPG	Burke, Petersilka, and Gross
BSE	Bethe-Salpeter equation
BTE	Boltzmann transport equation
c	Correlation
CEDA	Common energy denominator approximation
CEO	Collective electronic oscillator
CIS	Configuration Interaction Singles
CN	Crank and Nicholson
CREI	Charge Resonance Enhanced Ionization
CVD	Chemical vapor deposition
DFT	Density functional theory
DODS	Different Orbitals for Different Spins
EM	Exponential midpoint
ETRS	Enforced time-reversal symmetry
EXX	Exact exchange
FWHM	Full width at half maximum
GGA	Generalized gradient approximation
GGG	Gonze, Ghosez, and Godby
GK	Gross and Kohn