Lecture Notes in Physics

Springer
Berlin
Heidelberg
New York
Barcelona
Hong Kong
London
Milan
Paris
Tokyo

Physics and Astronomy ONLINE LIBRARY
http://www.springer.de/phys/

The Editorial Policy for Edited Volumes

The series *Lecture Notes in Physics* (LNP), founded in 1969, reports new developments in physics research and teaching - quickly, informally but with a high degree of quality. Manuscripts to be considered for publication are topical volumes consisting of a limited number of contributions, carefully edited and closely related to each other. Each contribution should contain at least partly original and previously unpublished material, be written in a clear, pedagogical style and aimed at a broader readership, especially graduate students and nonspecialist researchers wishing to familiarize themselves with the topic concerned. For this reason, traditional proceedings cannot be considered for this series though volumes to appear in this series are often based on material presented at conferences, workshops and schools.

Acceptance

A project can only be accepted tentatively for publication, by both the editorial board and the publisher, following thorough examination of the material submitted. The book proposal sent to the publisher should consist at least of a preliminary table of contents outlining the structure of the book together with abstracts of all contributions to be included. Final acceptance is issued by the series editor in charge, in consultation with the publisher, only after receiving the complete manuscript. Final acceptance, possibly requiring minor corrections, usually follows the tentative acceptance unless the final manuscript differs significantly from expectations (project outline). In particular, the series editors are entitled to reject individual contributions if they do not meet the high quality standards of this series. The final manuscript must be ready to print, and should include both an informative introduction and a sufficiently detailed subject index.

Contractual Aspects

Publication in LNP is free of charge. There is no formal contract, no royalties are paid, and no bulk orders are required, although special discounts are offered in this case. The volume editors receive jointly 30 free copies for their personal use and are entitled, as are the contributing authors, to purchase Springer books at a reduced rate. The publisher secures the copyright for each volume. As a rule, no reprints of individual contributions can be supplied.

Manuscript Submission

The manuscript in its final and approved version must be submitted in ready to print form. The corresponding electronic source files are also required for the production process, in particular the online version. Technical assistance in compiling the final manuscript can be provided by the publisher's production editor(s), especially with regard to the publisher's own LaTeX macro package which has been specially designed for this series.

LNP Homepage (http://link.springer.de/series/lnp/)

On the LNP homepage you will find:
–The LNP online archive. It contains the full texts (PDF) of all volumes published since 2000. Abstracts, table of contents and prefaces are accessible free of charge to everyone. Information about the availability of printed volumes can be obtained.
–The subscription information. The online archive is free of charge to all subscribers of the printed volumes.
–The editorial contacts, with respect to both scientific and technical matters.
–The author's / editor's instructions.

C. Fiolhais F. Nogueira M. Marques (Eds.)

A Primer in Density Functional Theory

Springer

Editors

Carlos Fiolhais
Departamento de Física,
Universidade de Coimbra,
Rua Larga,
3004 -- 516, Coimbra, Portugal

Miguel A. L. Marques
Donostia International Physics Center
(DIPC),
P. Manuel Lardizábal 4,
20080 San Sebastián, Spain

Fernando Nogueira
Departamento de Física,
Universidade de Coimbra,
Rua Larga,
3004 -- 516, Coimbra, Portugal

Cataloging-in-Publication Data applied for

A catalog record for this book is available from the Library of Congress.

Bibliographic information published by Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at http://dnb.ddb.de

ISSN 0075-8450
ISBN 3-540-03082-2 Springer-Verlag Berlin Heidelberg New York

Springer-Verlag Berlin Heidelberg New York
a member of BertelsmannSpringer Science+Business Media GmbH

http://www.springer.de

Printed in Germany

Typesetting: Camera-ready by the authors/editor
Camera-data conversion by Steingraeber Satztechnik GmbH Heidelberg
Cover design: *design & production*, Heidelberg

Printed on acid-free paper
54/3141/du - 5 4 3 2 1 0

Preface

Density functional theory is a clever way to solve the Schrödinger equation for a many-body system. In the formulation given by Kohn, Hohenberg, and Sham in the 1960's the real system is described by an effective one-body system. To achieve that goal, the complex many-body wave function, which is the solution of the Schrödinger equation, is abandoned in favour of the density which only depends on the three spatial coordinates. The energy is just a function of this function, i.e., a density functional.

This book, which intends to be an introduction to density functional theory, collects the lectures presented in the second Coimbra School on Computational Physics. In a way, it is a sequel to the sold-out Lecture Notes in Physics vol. 500 (ed. D. Joubert). This Summer School took place in late August of 2001 in the nice scenery of the Caramulo mountains, in central Portugal, some 50 km away from the old University of Coimbra. It was organized by the recently established (1998) Center for Computational Physics of the University of Coimbra, and was the second of a series which started, in 1999, with a school on "Monte Carlo Methods in Physics".

Like the summer school in South-Africa which originated the volume 500, the Coimbra School on Computational Physics devoted to density functional methods was a good opportunity for graduate students to enter the realm of density functionals, or to enlarge their previous knowledge in this fast expanding branch of physics and chemistry. About 50 students from different countries attended the School. Some teachers, who were also present at the South-African School (John Perdew, Reiner Dreizler and Eberhard Gross), were joined by new ones (Eberhard Engel, Rex Godby, Fernando Nogueira and Miguel Marques). The school was possible due to the support of Fundação para a Ciência e Tecnologia, Fundação Calouste Gulbenkian and the University of Coimbra, whom we would like to acknowledge here.

The contents of this volume are as follows. The theoretical foundations of the theory are reviewed by Stefan Kurth and John Perdew, in a chapter which is essentially an updated version of the article published in the above mentioned volume 500. The recent orbital dependent functionals are presented by Eberhard Engel. Two important extensions to the standard theory follow: relativistic systems, by Reiner Dreizler; and time-dependent non-relativistic problems by Miguel Marques and Eberhard Gross. In the next chapter Rex

Godby and Pablo García-González discuss some of the shortcomings of density functional theory and contrast it with conventional many-body theory. A tutorial, by Fernando Nogueira, Alberto Castro, and Miguel Marques, on practical applications of the formalism to atoms, molecules, and solids closes this book.

From the school and from this book emerges the view that, even though the "divine functional" – the energy functional with exact exchange and exact correlation – is yet a vision far on the horizon, extraordinary progress has been made since the seminal works of Kohn, Hohenberg, and Sham (not to speak about the early work in the thirties by Thomas and Fermi). The local density approximation to exchange and correlation from the sixties has been surpassed by the now standard generalized-gradient approximations. In principle more precise approaches like the meta-generalized gradient approximation or hybrid functionals are now being developed and applied, climbing what John Perdew called picturesquely "Jacob's Ladder" towards the "divine functional". The Chemistry Nobel prize awarded in 1998 to John Pople and Walter Kohn indeed gave a major impulse to the dissemination of density functional theory in physics and chemistry (several applications in biology and geology have also appeared!), but in order to have "chemical accuracy" further steps have to be taken.

It is the task of the new generation to continue the past and present efforts in this exciting field. We hope with this "primer" in density functional theory to provide students, and even established researchers, an overview of the present state and prospects of density functional methods.

Last but not least, the Coimbra school was also an opportunity to recognize the work of an active player in the field – Reiner Dreizler – on the occasion of his retirement, which took place in September 2001. The organizers would like to dedicate the present book to him. Although they know that he is not keen of homages and that his activity in physics is not over, we think that it is fully justified to summarize here his curriculum, emphasizing some of his achievements.

Reiner Dreizler was born 1936 in Stuttgart, Germany. In 1961, he received his "Diploma" in theoretical physics at the Albert Ludwigs Universität, in Freiburg, and in 1964, the title of Doctor of Philosophy in theoretical physics at the Australian National University, Canberra. From 1964 to 1966 he was Research Associate at the University of Pennsylvania, Philadelphia, USA and thereafter, until 1972, Assistant Professor of Physics at the same University. From 1972 to his retirement, he was Full Professor of Theoretical Physics at the Johann Wolfgang Goethe Universität, Frankfurt am Main, Germany. He has been guest lecturer all around the world, namely in Romania, Australia, Portugal, Russia, Ukraine, Japan, the USA and Brazil. Regarding positions and honours: He was Dean in 1981/1982 of the Faculty of Physics, Universität Frankfurt, and became Fellow of the American Physical Society in 1995; In 1999 he received the endowed chair "S. Lyson Professor der Physik".

His research interests have been very diverse. Besides the development and application of density functional methods, he studied the many-body problem in nuclear, atomic and molecular physics, and the theory of atomic scattering processes. He also investigated variational, iterative and projective techniques in handling quantum-mechanical problems and made contributions to the quantum-field description of many-body systems. Over the years he accumulated more than 230 contributions to refereed journals, 27 conference contributions, and four books. These include two Plenum Press Proceedings volumes, that stemmed from schools on density functinal theory (one of them in Alcabideche, Lisbon), and the famous Springer texbook on density functional theory co-authored by his ex-student and friend Eberhard Gross. He was supervisor of many PhDs. (including one of the school organizers and two of the school speakers) and Diploma theses.

In a world where science is more and more specialized, it is more and more difficult to meet someone like Reiner Dreizler, who covered with his work the whole spectrum of quantum mechanics from Particle to Solid State Physics, through Atomic, Molecular and Cluster Physics. May his example be followed by others!

Coimbra,
December 2002

Carlos Fiolhais
Fernando Nogueira
Miguel Marques

List of Contributors

Alberto Castro
Departamento de Física Teórica,
Universidad de Valladolid,
47011 Valladolid, Spain
alberto.castro@tddft.org

Reiner Dreizler
Institut für Theoretische Physik,
J. W. Goethe - Universität Frankfurt
Robert-Mayer-Straße 6-8,
60054 Frankfurt/Main, Germany
dreizler@th.physik.
uni-frankfurt.de

Eberhard Engel
Institut für Theoretische Physik,
J. W.Goethe - Universität Frankfurt
Robert-Mayer-Straße 6-8,
60054 Frankfurt/Main, Germany
engel@th.physik.uni-frankfurt.de

Carlos Fiolhais
Departamento de Física,
Universidade de Coimbra,
Rua Larga,
3004 – 516, Coimbra, Portugal
tcarlos@teor.fis.uc.pt

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

Rex W. Godby
Department of Physics,
University of York,
Heslington, York YO10 5DD,
United Kingdom
rwg3@york.ac.uk

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

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

Miguel A. L. Marques
Donostia International Physics
Center (DIPC),
P. Manuel Lardizábal 4,
20080 San Sebastián, Spain
marques@tddft.org

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

John P. Perdew
Department of Physics and Quantum
Theory Group,
Tulane University, New Orleans
LA 70118, USA
perdew@frigg.phy.tulane.edu

Table of Contents

1 Density Functionals for Non-relativistic Coulomb Systems in the New Century
John P. Perdew, Stefan Kurth 1

1.1 Introduction 1
1.1.1 Quantum Mechanical Many-Electron Problem 1
1.1.2 Summary of Kohn–Sham Spin-Density Functional Theory . . . 2
1.2 Wavefunction Theory 5
1.2.1 Wavefunctions and Their Interpretation 5
1.2.2 Wavefunctions for Non-interacting Electrons 7
1.2.3 Wavefunction Variational Principle 8
1.2.4 Hellmann–Feynman Theorem 9
1.2.5 Virial Theorem 10
1.3 Definitions of Density Functionals 11
1.3.1 Introduction to Density Functionals 11
1.3.2 Density Variational Principle 12
1.3.3 Kohn–Sham Non-interacting System 13
1.3.4 Exchange Energy and Correlation Energy 14
1.3.5 Coupling-Constant Integration 16
1.4 Formal Properties of Functionals 20
1.4.1 Uniform Coordinate Scaling 20
1.4.2 Local Lower Bounds 22
1.4.3 Spin Scaling Relations 23
1.4.4 Size Consistency 23
1.4.5 Derivative Discontinuity 24
1.5 Uniform Electron Gas 25
1.5.1 Kinetic Energy 25
1.5.2 Exchange Energy 26
1.5.3 Correlation Energy 27
1.5.4 Linear Response 29
1.5.5 Clumping and Adiabatic Connection 32
1.6 Local, Semi-local and Non-local Approximations 32

1.6.1 Local Spin Density Approximation 32
1.6.2 Gradient Expansion 36
1.6.3 History of Several Generalized Gradient Approximations 40
1.6.4 Construction of a "GGA Made Simple" 42
1.6.5 GGA Nonlocality: Its Character, Origins, and Effects 44
1.6.6 Hybrid Functionals 49
1.6.7 Meta-generalized Gradient Approximations 50
1.6.8 Jacob's Ladder of Density Functional Approximations 51

2 Orbital-Dependent Functionals for the Exchange-Correlation Energy: A Third Generation of Density Functionals
Eberhard Engel 56

2.1 Introduction 56
2.1.1 Preliminaries and Notation 57
2.1.2 Motivation for Orbital-Dependent Functionals 59
2.1.3 Basic Concept of Orbital-Dependent Functionals 63
2.2 Optimized Potential Method (OPM) 64
2.2.1 Direct Functional Derivative 65
2.2.2 Total Energy Minimization 66
2.2.3 Invariance of the Density 67
2.2.4 Exact Relations Related to OPM 70
2.2.5 Krieger–Li–Iafrate Approximation 71
2.3 Exchange-Only Results 73
2.3.1 Accuracy of the KLI Approximation 73
2.3.2 Properties of the Exact Exchange: Comparison with Explicit Density Functionals 81
2.4 First-Principles Implicit Correlation Functionals 90
2.4.1 Many-Body Theory on the Basis of the Kohn–Sham System: Exact Expression for E_{xc} 90
2.4.2 Perturbative Approach to the Sham–Schlüter Equation: Second Order Correlation Functional 94
2.4.3 Extensions of the Second Order Functional 97
2.5 Semi-empirical Orbital-Dependent Exchange-Correlation Functionals 99
2.5.1 Self-interaction Corrected LDA 99
2.5.2 Colle–Salvetti Functional 100
2.6 Analysis of the Orbital-Dependent Correlation 101
2.6.1 Description of Dispersion Forces by Second Order Correlation Functional 101
2.6.2 Comparison of Available Orbital-Dependent Approximations for E_{c} 106
2.6.3 Analysis of the Second Order Correlation Potential 111
2.7 Final Remarks 117

3 Relativistic Density Functional Theory
Reiner Dreizler 123

3.1 Summary 123
3.2 Foundations 126
3.3 Functionals 129
3.4 Results 136
3.5 Further Results 140

4 Time-Dependent Density Functional Theory
Miguel A.L. Marques, Eberhard K.U. Gross 144

4.1 Introduction 144
4.2 Time-Dependent DFT 145
4.2.1 Preliminaries 145
4.2.2 The Runge–Gross Theorem 148
4.2.3 Time-Dependent Kohn–Sham Equations 151
4.2.4 XC Functionals 153
4.2.5 Numerical Considerations 156
4.3 Linear Response Theory 158
4.3.1 Basic Theory 158
4.3.2 The XC Kernel 161
4.4 Excitation Energies 164
4.4.1 DFT Techniques to Calculate Excitations 164
4.4.2 Full Solution of the Kohn–Sham Equations 166
4.4.3 Excitations from Linear-Response Theory 168
4.4.4 When Does It Not Work? 173
4.5 Atoms and Molecules in Strong Laser Fields 174
4.5.1 What Is a "Strong" Laser? 174
4.5.2 High-Harmonic Generation 176
4.5.3 Multi-photon Ionization 177
4.5.4 Ionization Yields from TDDFT 179
4.6 Conclusion 181

5 Density Functional Theories and Self-energy Approaches
Rex W. Godby, Pablo García-González 185

5.1 Introduction 185
5.2 Many-Body Perturbation Theory 186
5.2.1 Green's Function and Self-energy Operator 186
5.2.2 Many-Body Perturbation Theory and the GW Approximation 189
5.3 Pathologies of the Kohn–Sham xc Functional 194
5.3.1 The Band Gap Problem 196
5.3.2 Widely Separated Open Shell Atoms 199
5.3.3 The Exchange-Correlation Electric Field 200
5.4 Total Energies from Many-Body Theory 203

5.4.1 Theoretical Background 203
5.4.2 Applications 207
5.4.3 Generalised KS Schemes and Self-energy Models 212
5.5 Concluding Remarks 214

6 A Tutorial on Density Functional Theory
Fernando Nogueira, Alberto Castro, Miguel A.L. Marques 218

6.1 Introduction 218
6.2 Solving the Kohn–Sham Equations 219
6.2.1 Generalities 219
6.2.2 Atoms 224
6.2.3 Plane-Waves 225
6.2.4 Real-Space 229
6.3 Pseudo-potentials 230
6.3.1 The Pseudo-potential Concept 230
6.3.2 Empirical Pseudo-potentials 232
6.3.3 *Ab-initio* Pseudo-potentials 233
6.3.4 Hamann Potential 234
6.3.5 Troullier–Martins Potential 235
6.3.6 Non-local Core Corrections 236
6.3.7 Pseudo-potential Transferability 237
6.3.8 Kleinman and Bylander Form of the Pseudo-potential 238
6.4 Atomic Calculations 239
6.5 Plane-Wave Calculations 244
6.6 Real-Space Calculations 251