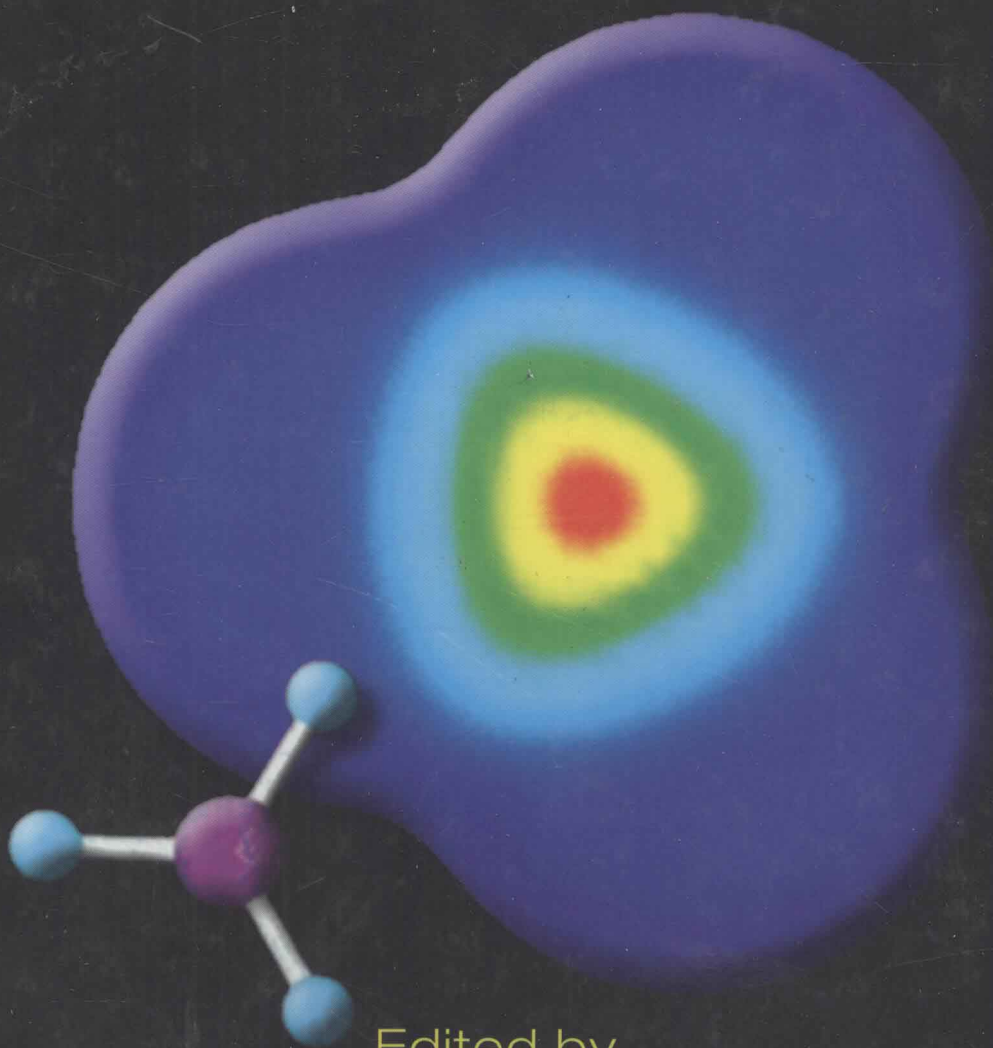


Chemical Reactivity Theory

A Density Functional View



Edited by
Pratim Kumar Chattaraj



CRC Press
Taylor & Francis Group

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Boca Raton London New York

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Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-1-4200-6543-5 (Hardcover)

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Library of Congress Cataloging-in-Publication Data

Chattaraj, Pratim Kumar.

Chemical reactivity theory : a density functional view / Pratim Kumar
Chattaraj.
p. cm.

Includes bibliographical references and index.

ISBN 978-1-4200-6543-5 (hardcover : alk. paper)

1. Density functionals. 2. Electron distribution. 3. Chemical reaction,
Conditions and laws of. I. Title.

QD462.6.D45C43 2009

541'.394--dc22

2008054117

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Chemical Reactivity Theory

A Density Functional View

Preface

Chemical reactions take place due to the redistribution of electron density among the reacting partners. Focusing on changes in electron density, which accompany the breaking and forming of chemical bonds, instead of the changes in the wave function accompanying them, allows us to use the “classical” three-dimensional language. Conceptual density functional theory (DFT) quantifies the possible responses of the system to various changes in density. Popular concepts like electronegativity, hardness, and electrophilicity, which explain a large number of diverse types of reactions in a systematic fashion, are grounded in conceptual DFT.

The aim of this book is to introduce various aspects of DFT and their connections to a chemical reactivity theory at a broadly accessible level. To this end, 34 chapters have been written by 65 eminent scientists from 13 different countries. Although the book is designed for readers with little or no prior knowledge of the subject, the breadth of the book and the expertise of the authors ensure that even experienced scientists will benefit from its contents.

The book comprises chapters on bonding, interactions, reactivity, dynamics, toxicity, and aromaticity as well as fundamental aspects of DFT. Several chapters are minireviews of the key global and local reactivity descriptors and their variations under different perturbations.

I am grateful to all the authors and the reviewers who cooperated with me to ensure the publication of the book on time. It is a great pleasure to express my gratitude to my teachers, Professors S.C. Rakshit, B.M. Deb, and R.G. Parr, for kindly introducing me to the fascinating field of quantum mechanics as applied to many-electron systems. I would especially like to thank Professor Paul Ayers, Lance Wobus, David Fausel, and Santanab Giri. Finally, I must express my gratitude to my wife Samhita and my daughter Saparya for their wholehearted support.

Pratim Kumar Chattaraj

Editor



Pratim Kumar Chattaraj joined the faculty of IIT Kharagpur after obtaining his BSc and MSc from Burdwan University and his PhD from the Indian Institute of Technology (IIT) Bombay. He is now a professor and the head of the department of chemistry and also the convener of the Center for Theoretical Studies at IIT Kharagpur. He was a postdoctoral research associate at the University of North Carolina at Chapel Hill and has served as a visiting professor to several other universities throughout the world. Apart from teaching, Professor Chattaraj is involved in research on density functional theory, the theory of chemical reactivity, *ab initio* calculations, quantum trajectories, and nonlinear dynamics. He has

been invited to deliver special lectures at several international conferences and to contribute chapters to many edited volumes. Professor Chattaraj is a member of the editorial board of the *Journal of Molecular Structure (Theochem)* and the *Journal of Chemical Sciences*, among others. He is a council member of the Chemical Research Society of India and a fellow of the Indian Academy of Sciences (Bangalore, India) and the Indian National Science Academy (New Delhi, India).

Contributors

Paul W. Ayers

Department of Chemistry
McMaster University
Hamilton, Ontario, Canada

P. Balanarayan

Department of Chemistry
University of Pune
Pune, Maharashtra, India

Libero J. Bartolotti

Department of Chemistry
East Carolina University
Greenville, North Carolina

Subhash C. Basak

Center for Water and Environment
Natural Resources Research Institute
University of Minnesota Duluth
Duluth, Minnesota

Josep Maria Bofill

Departament de Química Orgànica
Universitat de Barcelona i Parc Científic
de Barcelona
Barcelona, Spain

Alexander I. Boldyrev

Department of Chemistry and
Biochemistry
Utah State University
Logan, Utah

Patrick Bultinck

Department of Inorganic and Physical
Chemistry
Ghent University
Ghent, Belgium

Ramon Carbó-Dorca

Department of Inorganic and Physical
Chemistry
Ghent University
Ghent, Belgium

and

Department of Chemistry
Institute of Computational Chemistry
University of Girona
Girona, Spain

Andrés Cedillo

Departamento de Química
Universidad Autónoma Metropolitana-
Iztapalapa
Mexico City, México

Asit K. Chandra

Department of Chemistry
North-Eastern Hill University
Shillong, Meghalaya, India

P. K. Chattaraj

Department of Chemistry and Center
for Theoretical Studies
Indian Institute of Technology
Kharagpur, West Bengal, India

Abhijit Chatterjee

Material Science
Accelrys KK
Tokyo, Japan

Sofie Van Damme

Department of Inorganic and Physical
Chemistry
Ghent University
Ghent, Belgium

Susmita De

Department of Inorganic and Physical
Chemistry
Indian Institute of Science
Bangalore, Karnataka, India

B. M. Deb

Indian Institute of Science Education
and Research
Kolkata, West Bengal, India

P. Fuentealba

Departamento de Física
Facultad de Ciencias
Universidad de Chile
Santiago, Chile

Shridhar R. Gadre

Department of Chemistry
University of Pune
Pune, Maharashtra, India

Marcelo Galván

Departamento de Química
División de Ciencias Básicas
e Ingeniería
Universidad Autónoma Metropolitana-
Iztapalapa
Mexico City, México

Jorge Garza

Departamento de Química
División de Ciencias Básicas
e Ingeniería
Universidad Autónoma Metropolitana-
Iztapalapa
Iztapalapa, México

José L. Gázquez

Departamento de Química
División de Ciencias Básicas
e Ingeniería
Universidad Autónoma Metropolitana-
Iztapalapa
Mexico City, México

Paul Geerlings

Eenheid Algemene Chemie
Faculty of Sciences
Free University of Brussels
Brussels, Belgium

Swapan K. Ghosh

Theoretical Chemistry Section
Bhabha Atomic Research Centre
Mumbai, Maharashtra, India

Xavier Giménez

Departament de Química Física
Universitat de Barcelona i Parc Científic
de Barcelona
Barcelona, Spain

S. Giri

Department of Chemistry and Center
for Theoretical Studies
Indian Institute of Technology
Kharagpur, West Bengal, India

D. Guerra

Department of Chemistry
Universidad Técnica Federico
Santa María
Valparaíso, Chile

Brian D. Gute

Center for Water and Environment
Natural Resources Research Institute
University of Minnesota Duluth
Duluth, Minnesota

Soledad Gutiérrez-Oliva

Laboratorio de Química Teórica
Computacional
Facultad de Química
Pontificia Universidad Católica
de Chile
Santiago, Chile

Manoj K. Harbola

Department of Physics
Indian Institute of Technology
Kanpur, Uttar Pradesh, India

Eluvathingal D. Jemmis

Indian Institute of Science Education
and Research
CET Campus
Tiruvananthapuram, Tamil Nadu, India

Rahul Kar

Physical Chemistry Division
National Chemical Laboratory
Pune, Maharashtra, India

P. Kolandaivel

Department of Physics
Bharathiar University
Coimbatore, Tamil Nadu,
India

György Lendvay

Institute of Structural Chemistry
Chemical Research Center
Hungarian Academy of Sciences
Budapest, Hungary

M. Levy

Department of Chemistry
Duke University
Durham, North Carolina

Shubin Liu

Research Computing Center
Renaissance Computing Institute
University of North Carolina
Chapel Hill, North Carolina

Eduard Matito

The Lundbeck Foundation Center
for Theoretical Chemistry
Department of Chemistry
University of Aarhus
Aarhus, Denmark

Denise Mills

Center for Water and Environment
Natural Resources Research Institute
University of Minnesota Duluth
Duluth, Minnesota

Salvador Miret-Artés

Department of Atomic, Molecular,
and Cluster Physics
Instituto de Física Fundamental
Consejo Superior de Investigaciones
Científicas
Madrid, Spain

Jane S. Murray

Department of Chemistry
University of New Orleans
New Orleans, Louisiana
and

Department of Chemistry
Cleveland State University
Cleveland, Ohio

Á. Nagy

Department of Theoretical Physics
University of Debrecen
Debrecen, Hungary

Roman F. Nalewajski

Department of Theoretical Chemistry
Jagiellonian University
Cracow, Poland

Ramanathan Natarajan

Department of Chemical Engineering
Lakehead University
Thunder Bay, Ontario, Canada

Minh Tho Nguyen

Department of Chemistry
Mathematical Modeling and
Computational Science Center
University of Leuven
Leuven, Belgium

Sourav Pal

Physical Chemistry Division
National Chemical Laboratory
Pune, Maharashtra, India

Robert G. Parr

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina

Ralph G. Pearson

Chemistry and Biochemistry
Department
University of California
Santa Barbara, California

Jordi Poater

Institut de Química Computacional
and Departament de Química
Universitat de Girona
Girona, Spain

Peter Politzer

Department of Chemistry
University of New Orleans
New Orleans, Louisiana

and

Department of Chemistry
Cleveland State University
Cleveland, Ohio

Paul Popelier

Manchester Interdisciplinary Biocenter
University of Manchester
Manchester, United Kingdom

Frank De Proft

Eenheid Algemene Chemie
Vrije Universiteit Brussel
Brussels, Belgium

D. R. Roy

Department of Chemistry and Center
for Theoretical Studies
Indian Institute of Technology
Kharapur, West Bengal, India

Ángel S. Sanz

Department of Atomic, Molecular,
and Cluster Physics
Instituto de Física Fundamental
Consejo Superior de Investigaciones
Científicas
Madrid, Spain

G. Narahari Sastry

Molecular Modeling Group
Indian Institute of Chemical Technology
Hyderabad, Andhra Pradesh, India

A. Savin

Laboratoire de Chimie Theorique
CNRS et Universite Pierre et Marie
Curie Paris VI
Paris, France

Paul von Ragué Schleyer

Department of Chemistry and Center
for Computational Chemistry
University of Georgia
Athens, Georgia

K. D. Sen

School of Chemistry
University of Hyderabad
Hyderabad, Andhra Pradesh, India

Patrick Senet

Institut Carnot de Bourgogne
UMR 5209 CNRS-Université
de Bourgogne
Dijon, France

Alina P. Sergeeva

Department of Chemistry and
Biochemistry
Utah State University
Logan, Utah

Miquel Solà

Institut de Química Computacional
and Departament de Química
Universitat de Girona
Girona, Spain

V. Subramanian

Chemical Laboratory
Central Leather Research Institute
Chennai, Tamil Nadu, India

Alejandro Toro-Labbé

Laboratorio de Química Teórica
Computacional
Facultad de Química
Pontificia Universidad Católica de Chile
Santiago, Chile

David J. Tozer

Department of Chemistry
University of Durham
Durham, United Kingdom

Rubicelia Vargas

Departamento de Química
División de Ciencias Básicas
e Ingeniería
Universidad Autónoma Metropolitana-
Iztapalapa
Mexico City, México

P. Venuvanalingam

School of Chemistry
Bharathidasan University
Tiruchirapalli, Tamil Nadu, India

Weitao Yang

Department of Chemistry
Duke University
Durham, North Carolina

Dmitry Yu. Zubarev

Department of Chemistry and
Biochemistry
Utah State University
Logan, Utah

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1 How I Came about Working in Conceptual DFT

Robert G. Parr

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When Pratim Chattaraj asked me to provide some kind of “foreword” to this book, my first reaction was “no,” since everyone knows that the past is not so important in science and that one person’s recollections often are faulty. What we had here was just a long-laboring quantum chemist with a rigorous training in classical Gibbsian chemical thermodynamics, always enchanted with the chemical potential. So when quantum chemistry was suddenly confronted with the density functional theory (DFT), I was ready and happy to plunge into work with DFT, the chemical potential again taking a central role. To say a little more, below is reproduced a short piece which I provided for a 2003 Springer book entitled *Walter Kohn* (two photographs which were in the original are omitted). What this contains is the story of how DFT came into chemistry proper, broadening computational chemistry and enlightening chemical concepts both old and new. Concepts are what this volume is mainly about: conceptual DFT.

1.1 BONDING OF QUANTUM PHYSICS WITH QUANTUM CHEMISTRY*

The bond that developed between quantum physics and quantum chemistry, that led to the award of a big chemistry prize to the physicist Walter Kohn in 1998, developed not without trial. Here I give an account of it. An element in this bond has been a friendship between Walter Kohn and me. My having reached 80 first, he has already kindly spoken of this [1]. Now it is my turn.

In the 20s and early 30s there was a flush of successes in establishing the ability of quantum mechanics to describe the simplest molecules accurately: the Born-Oppenheimer approximation, the nature of chemical bonding, and the fundamentals

* I thank Springer for allowing me to reproduce this article.

of molecular spectroscopy. But then the quantitative theory of molecular structure, which we call quantum chemistry, was stymied, by the difficulty of solving the Schrödinger equation for molecules. The senior chemical physicists of the 30s pronounced the problem unsolvable. But the younger theoreticians in the period coming out of WWII thought otherwise. Clearly one could make substantial progress toward the goal of complete solution, because the equation to solve was known and had a simple universal structure.

The boundary conditions too were known. It would not be as easy as handling an infinite periodic solid, but a number of us set to work. The special demand of chemistry was to quantify very small molecular changes. Successes came slowly, but with the development of computers and a lot of careful, clever work, by the 90s the quantitative problem was essentially solved. The emergent hero of the chemical community was John Pople, whose systematic strategy and timely method developments were decisive. The methods of what is termed “*ab initio*” quantum chemistry became available and used everywhere.

Over the years the quantum chemists did a lot more than gradually improve their ability to calculate wavefunctions and energies from Schrödinger’s equation. All the while they have served molecular spectroscopy, physical inorganic chemistry, and physical organic chemistry. Relevant for the present story was the development by Per-Olov Löwdin in 1955 of the density matrix reduction of the Schrödinger equation, especially the identification and mathematical physics of natural spin orbitals and their occupation numbers. The hope was, although hope floundered, that the Schrödinger problem could be resolved in terms of the first- and second-order density matrices. Foundering came because of the difficulty of incorporating the Pauli principle.

Beginning way back in the 20s, Thomas and Fermi had put forward a theory using just the diagonal element of the first-order density matrix, the electron density itself. This so-called statistical theory totally failed for chemistry because it could not account for the existence of molecules. Nevertheless, in 1968, after years of doing wonders with various free-electron-like descriptions of molecular electron distributions, the physicist John Platt wrote [2] “We must find an equation for, or a way of computing directly, total electron density.” [This was very soon after Hohenberg and Kohn, but Platt certainly was not aware of HK; by that time he had left physics.]

From the end of the 40s, I was a happy participant in most of these things, *ab initio* and the rest, although from about 1972 I became pretty much an observer. We plunged into density-functional theory.

DFT soon intoxicated me. There were the magnificent Hohenberg-Kohn and Kohn-Sham 1964–65 papers. The X α method of John Slater was popular in those days, but it was not sufficient for the high accuracy needed. And I was much taken by the work of Walter Kohn, whom I had known since 1951. There were many things to do: Improve upon the LDA to reach the accuracy needed for chemical applications. Shift the emphasis on fixed, very large electron number toward variable, small number, since that most concerns chemistry. Enlarge the language to include chemical as well as solid-state concepts. Introduce into DFT, as appropriate, some of the theoretical advances already made within quantum chemistry. All of these things subsequently came about. The methods and concepts of DFT became available and used throughout the chemical community.