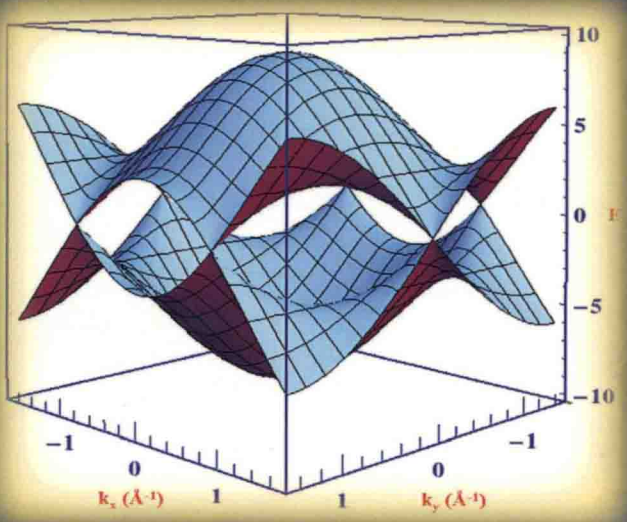
ATOMS, MOLECULES, AND CLUSTERS

CONCEPTS AND METHODS IN MODERN THEORETICAL CHEMISTRY

STATISTICAL MECHANICS



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SWAPAN KUMAR GHOSH
PRATIM KUMAR CHATTARAJ

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CONCEPTS AND METHODS IN MODERN THEORETICAL CHEMISTRY

STATISTICAL MECHANICS

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Structure, Reactivity, and Dynamics
Series Editor: Pratim Kumar Chattaraj

Aromaticity and Metal Clusters
Edited by Pratim Kumar Chattaraj

Concepts and Methods in Modern Theoretical Chemistry: Electronic Structure and Reactivity
Edited by Swapan Kumar Ghosh and Pratim Kumar Chattaraj

Concepts and Methods in Modern Theoretical Chemistry: Statistical Mechanics
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Quantum Trajectories
Edited by Pratim Kumar Chattaraj

Series Preface

ATOMS, MOLECULES, AND CLUSTERS: STRUCTURE, REACTIVITY, AND DYNAMICS

While atoms and molecules constitute the fundamental building blocks of matter, atomic and molecular clusters lie somewhere between actual atoms and molecules and extended solids. Helping to elucidate our understanding of this unique area with its abundance of valuable applications, this series includes volumes that investigate the structure, property, reactivity, and dynamics of atoms, molecules, and clusters.

The scope of the series encompasses all things related to atoms, molecules, and clusters including both experimental and theoretical aspects. The major emphasis of the series is to analyze these aspects under two broad categories: approaches and applications. The *approaches* category includes different levels of quantum mechanical theory with various computational tools augmented by available interpretive methods, as well as state-of-the-art experimental techniques for unraveling the characteristics of these systems including ultrafast dynamics strategies. Various simulation and quantitative structure–activity relationship (QSAR) protocols will also be included in the area of approaches.

The *applications* category includes topics like membranes, proteins, enzymes, drugs, biological systems, atmospheric and interstellar chemistry, solutions, zeolites, catalysis, aromatic systems, materials, and weakly bonded systems. Various devices exploiting electrical, mechanical, optical, electronic, thermal, piezoelectric, and magnetic properties of those systems also come under this purview.

The first two books in the series are (a) *Aromaticity and Metal Clusters* and (b) *Quantum Trajectories*. A two-book set on *Concepts and Methods in Modern Theoretical Chemistry*, edited by Swapan Kumar Ghosh and Pratim Kumar Chattaraj, is the new addition to this series. The first book focuses on the electronic structure and reactivity of many-electron systems and the second book deals with the statistical mechanical treatment of collections of such systems.

Pratim Kumar Chattaraj
Series Editor

Foreword

A certain age comes when it is no longer unseemly to reflect on one's contribution to the world and, in the case of a scientist, the mark one has left on one's career. Professor B. M. Deb has reached such an age and can look back with considerable satisfaction on his scientific legacy. I knew him long ago, when his career was still to come, when he was at Oxford and was forming his aspirations and skills. Now, long after, in these volumes, we are seeing where those aspirations and skills in due course led.

One of the principal contributions of theoretical chemistry to what might be called "everyday" chemistry is its development of powerful computational techniques. Once such techniques were regarded with suspicion and of little relevance. But in those days the techniques were primitive, and the hardware was barely adequate for the enormous computations that even the simplest molecules require. Then, over the decades, techniques of considerable sophistication emerged, and the hardware evolved in unimaginable ways to accommodate and inspire even more imagination and effort. Now, the computations give great insight and sometimes surpass even actual measurements.

Of these new techniques, the most intriguing, and currently one in high fashion, has been the density functional theory. That Professor Deb has contributed so much in this field is demonstrated by the number of contributions in these volumes that spring from his work. Fashions, of course, come and go, but these techniques are currently having a considerable impact on so many branches of chemistry that they are undoubtedly a good reason for Professor Deb to reflect, with characteristic but misplaced modesty, on what he has done to promote and advance the technique.

It was for me a great pleasure to know the young Professor Deb and to discern promise and to know that the contributions to these volumes show that that promise has been more than amply fulfilled in a lifetime of contributions to theoretical chemistry. Professor Deb must be enormously proud of having inspired these volumes, and justly so.

Peter Atkins
Oxford

Preface

This collection presents a glimpse of selected topics in theoretical chemistry by leading experts in the field as a tribute to Professor Bidyendu Mohan Deb in celebration of his seventieth birthday.

The research of Professor Deb has always reflected his desire to have an understanding and rationalization of the observed chemical phenomena as well as to predict new phenomena by developing concepts or performing computations with the help of available theoretical, modeling, or simulation techniques. Formulation of new and more powerful theoretical tools and modeling strategies has always formed an ongoing and integral part of his research activities. Proposing new experiments, guided by theoretical insights, has also constituted a valuable component of his research that has a fairly interdisciplinary flavor, having close interconnections with areas like physics and biology.

The concept of single-particle density has always fascinated him, perhaps starting with his work on force concept in chemistry, where the density is sufficient to obtain Hellmann–Feynman forces on the nuclei in molecules. His two reviews on "Force Concept in Chemistry" and "Role of Single Particle Density in Chemistry," published in *Reviews of Modern Physics*, have provided a scholarly exposition of the intricate concepts, inspiring tremendous interest and growth in this field. These have culminated in two edited books. The force concept provided the vehicle to go to new ways of looking at molecular shapes, the HOMO postulate being an example of his imaginative skills. The concept of forces on the nuclei was soon generalized to the concept of stress tensor within the electron cloud in molecules, the role of which in determining chemical binding and stability of molecules was also explored. Various aspects of the density functional theory (DFT) were investigated. The static aspects were soon viewed as only a special case of the corresponding dynamical theory, the so-called quantum fluid dynamics (QFD), which was developed in 3-D space and applied to study collision phenomena, response to external fields, and other related problems.

His mind has always opened new windows to bring in the fresh flavor of novel concepts for interpreting the "observed," predicting the "not yet observed," and also created tools and strategies to conquer unknown territory in the world of molecules, materials, and phenomena. "Concepts are the fragrance of science," he always emphasizes. His research has often seemed to be somewhat unconventional in the sense that he has always stressed conceptual developments that are often equally suited for practical applications as well. He has a thirst for looking into the secret of "why things are the way they are" and the mystery behind "being to becoming," focusing on the structure and dynamics of systems and phenomena, both of which have been enriched immensely by his contributions. Aptly, we have the two present books covering structure and dynamics, respectively.

The topics in *Concepts and Methods in Modern Theoretical Chemistry: Electronic Structure and Reactivity* include articles on DFT, particularly the functional and conceptual aspects, excited states, molecular electrostatic potentials, intermolecular

interactions, general theoretical aspects, application to molecules, clusters and solids, electronic stress, the information theory, the virial theorem, new periodic tables, the role of the ionization potential and electron affinity difference, etc. The majority of the chapters in *Concepts and Methods in Modern Theoretical Chemistry: Statistical Mechanics* include time-dependent DFT, QFD, photodynamic control, nonlinear dynamics, molecules in laser field, charge carrier mobility, excitation energy transfer, chemical reactions, quantum Brownian motion, the third law of thermodynamics, transport properties, nucleation, etc.

In the Indian context, theoretical chemistry has experienced significant growth over the years. Professor Deb has been instrumental in catalyzing this growth by providing the seed and nurturing young talents. It is the vision and effort of Professor Deb that made it possible to inspire the younger generation to learn, teach, and practice theoretical chemistry as a discipline. In this context, it is no exaggeration to describe him as the doyen of modern theoretical chemistry in India.

Professor Deb earned a PhD with Professor Charles Coulson at the University of Oxford and then started his professional career at the Indian Institute of Technology, Bombay, in 1971. Being a scientist–humanist of the highest order, he has always demanded a high sense of integrity and a deep involvement from his research group and other students. He has never sacrificed his own human qualities and never allowed other matters to overtake the human aspects of life.

While his research has focused on conceptual simplicity, computational economy, and sound interpretive aspects, his approach to other areas of life reflects the same. We have often wondered at the expanse of his creativity, which is not restricted to science but also covers art, literature, and life in general. His passion for work has, of course, never overshadowed his warmth, affection, and helpfulness to others. He has an extraordinary ability to act as a creative and caring mentor. His vast knowledge in science, art, literature, and many other of the finer aspects of life in general, together with his boundless sources of enthusiasm, creativity, and imagination, has often made him somewhat unconventional in his thinking, research, and teaching. Designing new experiments in class and introducing new methods in teaching have also been his passion. His erudition and versatility are also reflected in his writings on diverse topics like the cinema of Satyajit Ray and lectures on this as well as various aspects of art.

We are privileged to serve as editors of these two books on Concepts and Methods in Modern Theoretical Chemistry and offer the garland of scholarly essays written by experts as a dedication to this great scientist–humanist of recent times with affection and a deep sense of respect and appreciation for all that he has done for many of us and continues to do so. We also gratefully acknowledge the overwhelming and hearty response received from the contributors, to whom we express our indebtedness.

We are grateful to all the students, associates, and collaborators of Professor B. M. Deb who spontaneously contributed to the write-up of the "Reminiscences" and, in particular, Dr. Amlan K. Roy for compiling it in a coherent manner to the present form. Finally, we are deeply indebted to Professor B. M. Deb for his kind help, guidance, and encouragement throughout our association with him.

Swapan Kumar Ghosh
Pratim Kumar Chattaraj

Reminiscences

It is indeed a great pleasure to pen this note in celebration of Professor B. M. Deb's seventieth birthday. For many of us, he is a mentor, confidante, and adviser. Many others look at him as an extraordinary teacher; a patient, encouraging, and motivating guide; a warm and caring human being; and a connoisseur of literature, art, and so on. His dedication and passion for science is infectious.

Many of us have been fortunate to attend his lectures on quantum chemistry, structure, bonding, symmetry, and group theory, which were all about the interlinking of abstract concepts that are often sparsely scattered. After trudging along a series of lectures, one is rewarded with the eventual conclusion that all chemical bonds are mere manifestations of a single phenomenon, namely, the redistribution of electron density. Often, he would explain physics from real-life analogies rather than try to baffle and intimidate audiences with lots of mathematics—a popular trick often used in the community. Just paying attention in his class gives one enough confidence to tackle the most challenging problems in quantum chemistry. His recent endeavor to initiate a course on Indian heritage has been highly appreciated. It is not a history class, as the title may imply to some people, but rather a scientific evaluation of the Indian past. Taking examples from our glorious past, the course differentiates between easy and right about scientific ethics and logically establishes the path one should follow for uplifting individual souls and society as a whole. Although a theoretician, his enthusiasm and excitement for practical applications of science is no less. The experiments on beating hearts and chemical oscillations are among the most popular in the class.

His books *The Force Concept in Chemistry* and *The Single-Particle Density in Physics and Chemistry* were hugely influential among those who sought, in quantum chemistry, not just a computational tool for the calculation of molecular properties, but a fundamental understanding of the physics of chemical bonding and molecular reactivity. The application of the Hellmann–Feynman theorem to provide qualitative insights into chemical binding in molecules as well as molecular shapes caught the interest of even R. P. Feynman. As a research student, his communication with Professor Feynman was a matter of great amazement, motivation, and pride for many of his early PhD students, as Dr. Anjuli S. Bamzai recalls. Despite his considerable work in density functional theory (DFT), he held an agnostic attitude toward it, in the sense that he did not regard the search for a functional as the holy grail of DFT or see DFT as being somehow in opposition to wave function–based theories. He was also not against approximations and freely employed them wherever useful. But he was convinced that the electron density held the key to a deeper understanding of the chemical phenomena. Thus, in a way, he was willing to entertain the need for considering the phase in addition to density to achieve a consistent treatment of excited states and time-dependent phenomena.

To have worked with him has been a major turning point in our lives. We discover him as a scientist with high morality and professional ethics. It is not only

learning the concepts in theoretical chemistry but also a more holistic approach toward research, learning, and science itself. While scrupulously fair, he expected his students to be conscientious. He gave his all to his students and to his research. Reasonably enough, he expected no less from his students and from his colleagues, a favorite expression being that he wanted the students "to go flat out" on their prospective research problems. The amount of hard work that he put, propelled by tiny seeds of imagination and analytical logic, always inspired us. But while the force of his scientific conviction was strong, he was always open to arguments and discussion. Even in turbulent times and under less-than-ideal conditions, he was not willing to compromise on his scientific standards or integrity. He had a knack for choosing and working on problems that were emerging frontiers of theoretical chemistry. That was because of his intuition to choose research projects for us so that we could contribute to the field effectively, despite the fact that all his research works were done in India in relative isolation. Although much of his research career spanned the overlap between physics and chemistry, he had no sympathy for those who would regard chemistry as inferior to physics. When a physicist, after hearing Professor Deb speak about his current research, praised him with the words, "You are almost doing physics," he rejoined with a wry smile, "No, I am doing good chemistry." With this statement, even his detractors would agree!

It feels amazing that we have learned as much from anecdotal informal interaction with him as from the research experience. What added to the pleasure of working with him were discussions about science and nonscientific matters. It was fascinating to listen to him talk about poetry, literature, movies, food, art, and cultures across the world. We would occasionally visit his residence and spend time with him at the dining table discussing the progress of our projects while partaking of delicious snacks and meals prepared by Mrs. Deb. For many of us, it was something like a home away from home, and we soon learned that a combination of food and food for thought goes well together. The amazement of such an experience is narrated here by Dr. Bamzai. Their home was decorated with the works of some of the greatest artists of all time. Often one would come across a discussion about Leonardo da Vinci's *The Last Supper* or Picasso's *Guernica* and how the artist, through his work, had conveyed the tragedies of war and its horrific impact on innocent civilians. At other times, he would discuss how M. C. Escher's art effectively conveys important concepts such as symmetry and transformations in crystallography. He has serious concern also about science, culture, and heritage. He constantly engages into the popularization of science as well as the improvement of the education system in India. It is surprising how he was able to impart knowledge on such a diverse array of topics.

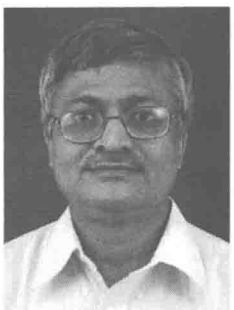
Given his varied interests and the positive energy that he imbues into his surroundings, we know that he will never stop being an academic. Despite his own and Mrs. Deb's deteriorating health, they have stood beside their students and colleagues with constant support and encouragement. Many of us remember the act of good Samaritan-ship by Professor Deb and his family toward his colleagues. One such act is vividly recollected here by Professor Harjinder Singh, whose daughter was struggling in an intensive care unit at that time. They needed to stay at a place close to the hospital. Deb's family extended their wholehearted support during that crisis, not

minding any inconvenience caused to them, especially when the city of Chandigarh was going through the political turmoil of a full-blown secessionist movement, regular terrorist threats, shootings, bus bombings, and assassinations.

A lesson we learned from Professor Deb that we have carried throughout our life was his admonition: "Beware of the fourth rater who calls the third rater good." It was a call and a challenge to aspire to the highest standards of excellence in life, and it is the pursuit of this gold standard that he strived to inculcate in us, despite potential temptations to discard it so often! We consider ourselves very fortunate to have Professor Deb as our teacher, philosopher, and guide. His work and work ethic will continue to influence and nurture future generations via many students and postdocs he has taught and guided. He remains a source of inspiration to all who wish to be an ideal teacher, a thorough researcher, and, above all, a decent human being. We feel privileged to be a part of his extended family and take this opportunity to express our sincere gratitude to him for his support, kindness, and patience. We are indebted to him and send our best wishes to his family.

Anjuli S. Bamzai
Pratim K. Chattaraj
Mukunda Prasad Das
Swapan K. Ghosh
Neetu Gupta
Geeta Mahajan
Smita Rani Mishra
Amitabh Mukherjee
Aniket Patra
Amlan K. Roy
Mainak Sadhukhan
R. P. Semwal
Harjinder Singh
Ranbir Singh
Nagamani Sukumar
Vikas
Amita Wadehra

Editors



Swapan Kumar Ghosh earned a BSc (Honors) and an MSc from the University of Burdwan, Bardhaman, India, and a PhD from the Indian Institute of Technology, Bombay, India. He did postdoctoral research at the University of North Carolina, Chapel Hill. He is currently a senior scientist with the Bhabha Atomic Research Centre (BARC), Mumbai, India, and head of its theoretical chemistry section. He is also a senior professor and dean-academic (Chemical Sciences, BARC) of the Homi Bhabha National Institute, Department of Atomic Energy (DAE), India, and an adjunct professor with the University of Mumbai–DAE Centre of Excellence in Basic Sciences, India.

He is a fellow of the Indian Academy of Sciences, Bangalore; Indian National Science Academy, New Delhi; National Academy of Sciences, India, Allahabad; Third World Academy of Sciences (TWAS), Trieste, Italy (currently known as the Academy of Sciences for the Developing World); and Maharashtra Academy of Sciences. He is a recipient of the TWAS prize in chemistry; silver medal of the Chemical Research Society of India (CRSI); the Jagdish Shankar Memorial Lecture Award of the Indian National Science Academy; the A. V. Rama Rao Prize of Jawarharlal Nehru Centre for Advanced Scientific Research, Bangalore, India; and the J. C. Bose Fellowship of the Department of Science and Technology, India. He is currently also one of the vice presidents of CRSI.

His research interests are theoretical chemistry, computational materials science, and soft condensed matter physics. He has been involved in teaching and other educational activities including the Chemistry Olympiad Program. He has twice been the mentor and delegation leader of the Indian National Chemistry Olympiad Team participating in the International Chemistry Olympiad at Athens (Greece) and Kiel (Germany).

Pratim Kumar Chattaraj earned a BSc (Honors) and an MSc from Burdwan University and a PhD from the Indian Institute of Technology (IIT), Bombay, India, and then joined the faculty of the IIT, Kharagpur, India. He is now a professor with the Department of Chemistry and also the convener of the Center for Theoretical Studies there. In the meantime, he visited the University of North Carolina, Chapel Hill, as a postdoctoral research associate and several other universities throughout the world as a visiting professor. Apart from teaching, Professor Chattaraj is involved in research on density functional theory, the theory of chemical reactivity, aromaticity in metal clusters, *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 *J. Mol. Struct. Theochem* (currently *Comp. Theo. Chem.*), *J. Chem. Sci., Ind. J. Chem.-A*, *Nature Collections Chemistry*, among others. He has edited three books and special issues of different journals. He was the head of the Department of Chemistry, IIT, Kharagpur, and a council member of the Chemical Research Society of India. He is a recipient of the University Gold Medal, Bardhaman Sammilani Medal, INSA Young Scientist Medal, B. C. Deb Memorial Award, B. M. Birla Science Prize, and CRSI Medal. He was an associate of the Indian Academy of Sciences. He is a fellow of the Indian Academy of Sciences (Bangalore), the Indian National Science Academy (New Delhi), the National Academy of Sciences, India (Allahabad), and the West Bengal Academy of Science and Technology. He is also a J. C. Bose National Fellow and a member of the Fonds Wetenschappelijk Onderzoek (FWO), Belgium.