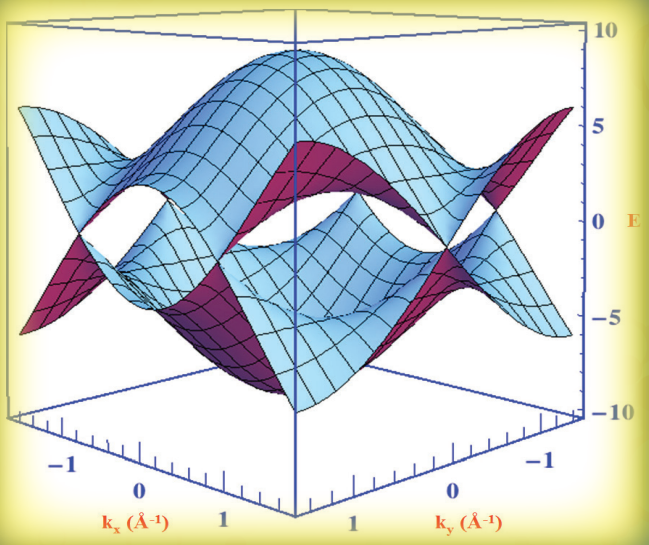
ATOMS, MOLECULES, AND CLUSTERS

CONCEPTS AND METHODS IN MODERN THEORETICAL CHEMISTRY

STATISTICAL MECHANICS



EDITED BY
SWAPAN KUMAR GHOSH
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CONCEPTS AND METHODS IN MODERN THEORETICAL CHEMISTRY

STATISTICAL MECHANICS

Atoms, Molecules, and Clusters
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
Edited by Swapan Kumar Ghosh and Pratim Kumar Chattaraj

Quantum Trajectories
Edited by Pratim Kumar Chattaraj

Atoms, Molecules, and Clusters

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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
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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.

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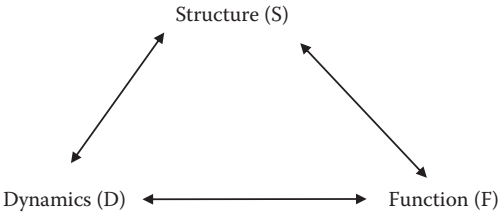
An Interview with B. M. Deb

(This interview was conducted by Richa Malhotra for the journal *Current Science*. An edited version of the interview was published in *Current Science* on January 25, 2012, and an expanded version appears in the present book. Courtesy of *Current Science*.)

- **How has the field of theoretical and computational chemistry evolved over the years?**

  One has to write a book to answer this! It is similar to answering how science has evolved in the last century and the present century so far. Let me try to explain how the broad contours of theoretical and computational chemistry have developed over many years.

  Theoretical chemistry has been operating at the interface between chemistry, physics, biology, mathematics, and computational science. It deals with *systems* and *phenomena* concerning these large subjects. The *systems* are microscopic, mesoscopic, and macroscopic, *viz.*, atoms, molecules, clusters, and other nanosystems, soft and hard condensed matter. The *phenomena* involve a holistic combination of *structure*, *dynamics*, and *function*. *Structure* concerns itself with geometry, where both Group Theory and Topology (especially, Graph Theory) come in. *Dynamics* deal with evolution in time; structure is a consequence of dynamics, and *vice versa*. *Function* implies all kinds of properties, *viz.,* electrical, magnetic, optical, chemical, biological, and even mechanical properties. Let me show this by a triangular SDF figure, which is actually *valid for every field of human endeavor,* including literature and arts.



The disciplines which study all of these are quantum chemistry (both nonrelativistic and relativistic), quantum biology and biochemistry, quantum pharmacology, spectroscopy, molecular reaction dynamics, equilibrium and nonequilibrium statistical mechanics, equilibrium and nonequilibrium thermodynamics, nonlinear dynamics, mathematical methods of chemistry, etc., with various subdisciplines. It is interesting to note that Graph Theory, which is a branch of mathematics and is also used by chemists, physicists, biologists, sociologists, electrical engineers, neural and other network scientists, had drawn primary inspiration in the 1870s from structural formulas in chemistry which denote *connectivity.* As you see, at this level, it is really not possible to distinguish between theoretical chemistry and theoretical physics or, for that matter, theoretical biology. Atomic and molecular physics, polymer and condensed matter physics—bringing in materials science—and even certain issues of structure and interaction in nuclear physics are of interest to theoretical chemists. Present-day mathematical chemistry, which uses topology—though not necessarily in conjunction with quantum mechanics—to develop quantitative structure–activity relations for drug design, hazard chemicals assessment, etc., is another aspect of theoretical chemistry.

Computational chemistry has been primarily concerned with the development and application of computer software, using theoretical chemistry methodologies, utilizing numerical methods and computer programming in a significant way. Nowadays, not all theoretical chemists and computational chemists develop their own codes. Only some do, if necessary, whereas others employ standard and/or commercially available software packages for performing computations on electronic structure; geometry; various chemical, physical, and biological properties; as well as various kinds of classical and semiclassical simulations of structures and dynamics of large molecular systems such as proteins, polymers, and liquids. Since the 1930s, theoretical and computational chemists have been a major driving force behind developments in computational sciences, including both computer hardware and software development, especially number crunching and graphics. Graphics are particularly important because chemists find it difficult to work without detailed visualization. Also, representing millions of computed numbers in terms of colorful pictures, which could undulate in time as well, greatly enhances our insight into the phenomenon being studied. Presently, we feel that any equation which cannot be solved analytically but the solution exists can be solved numerically with an accuracy

which goes beyond experimental accuracy as long as the variables are not too many in number.

Because of their subject's complex multidisciplinary nature, theoretical chemists have been somewhat like orphans! You can find them everywhere, in chemistry, biochemistry, physics, mathematics, computer science, chemical engineering, materials science, as well as in industries across the world, though I believe very few, if any at all, in Indian industries. Since earth scientists are currently using theoretical chemistry computations for interpretations of their data, perhaps we will soon have a theoretical chemist in an earth science department!

Historically, mathematicians, physicists, chemists, computer scientists, and even economists have contributed to theoretical chemistry. Apart from the mathematician J. Sylvester's realization in the 1870s that structural formulas in chemistry have a hidden algebraic structure, I think Gibbs's development of thermodynamics, followed by the axiomatic development of the subject by Carathéodory and Born, Debye–Hückel–Onsager theory of strong electrolytes, Lewis's electronic theory of valence, the vector atom model, etc., are some of the important landmarks in the early days of theoretical chemistry. Once quantum mechanics came into being, there resulted an explosive growth in the areas that I have mentioned earlier.

- **What have been your key contributions and areas of interest in chemistry?**

It is embarrassing to talk about "key contributions" of a mediocre scientist. I always believed that (1) theory should not only explain current experiment but should also make predictions for future experiment and that (2) concepts are the fragrance of science. Therefore, along with my research students, I have been struggling to develop rigorous concepts in chemistry which can lead to deep insights, as well as accurate results which are amenable to physical and pictorial interpretation. Whatever we have been able to do has been possible only because of my courageous students.

Because of my persistent interest in geometry, our first work in India was to develop a purely qualitative and general molecular–orbital approach (without computation and by using group theory extensively), leading to a force model for explaining and predicting various features of molecular geometry of small- and medium-sized molecules based on the electron density in the highest occupied molecular orbital. This was followed by semi-empirical computations of electronic structure and geometry of quite a few unknown molecules, predicting that they are capable of independent existence. Along with these, we wrote an article entitled "the force concept in chemistry." The responses to this article changed the course of our research, especially Fano's suggestion that we think of how the electron density can be calculated without the wave function and Feynman's suggestion that we look into internal stresses in molecules. Even though we did not know then of Hohenberg–Kohn theorems and Kohn–Sham equations, we were already completely convinced of the fundamental significance of electron density in three-dimensional space and strongly felt that, through the electron density, nonrelativistic quantum phenomena can have "classical"

interpretations, which are necessary for pictorial understanding. Based on Feynman's suggestion, we defined an electrostatic stress tensor using the electron density and showed that this has the same form as Maxwell's stress tensor for classical electromagnetic fields. Furthermore, along the bond direction in a diatomic molecule, the appropriate component of the stress tensor shows an extremum at the equilibrium internuclear distance. In trying to understand why stress tensor should be such an important entity, we realized that we have to go to classical fluid dynamics. The fluid dynamical interpretation of one-electron systems was already in existence but taking it to many-electron systems was rather difficult. We therefore developed what we called a quantum fluid dynamical interpretation of many-electron systems in terms of the electron density and defined a comprehensive stress tensor for such a system in terms of the full nonrelativistic Hamiltonian, i.e., by incorporating kinetic, electrostatic, exchange, and correlation terms. This still had the same form as Maxwell's tensor. We then defined a general criterion for the stability of matter, *viz.,* the force density obtained from this stress tensor must vanish at every point in three-dimensional space. The stress tensor, however, did not yield a deterministic equation for the electron density which has to incorporate both *space and time*.

Time was of the essence in our struggle. The two interlinked bottlenecks in the electron density approach were time dependence and excited states. We first developed a rigorous time-dependent density functional theory for a certain class of potentials by utilizing QFD. Since this version of density functional theory was not exact for all potentials, we also developed a similar approach in terms of natural orbitals which are exact in principle. This approach yielded an equation for the ground state density whose accuracy was very good. Using this, we calculated the frequency-dependent multipole (2^l-pole, l = 1, 2, 3, 4) polarizabilities of atoms. Some of these computed numbers still await experimental verification.

Efforts continued to generate more accurate equations for directly determining density by a single equation no matter how many electrons are there in the system. One such effort yielded a quadratic—rather than a differential—time-independent equation whose density yielded many interesting results. This equation led to an effort to justify the existence of empirically finite atomic, ionic, and Van der Waals radii—even though quantum mechanically these radii are infinite—by adopting a conjecture that such finite radii are decided by a single universal value of the electron density in space. Finally, we were able to obtain a fascinating nonrelativistic nonlinear single partial differential equation for the direct determination of electron density and properties of many-electron systems. Besides applying this equation to the ground state and time-dependent situations, application was also made to proton-atom high-energy scattering; it was possible to identify *approach, encounter, and departure regimes,* which should be helpful in chemical reactions. This equation has a number of interesting mathematical properties, some of which we have examined while others remain unexplored. A relativistic quantum fluid dynamical density approach was also

developed. Additionally, we have written quite a bit in trying to emphasize the fundamental significance of electron density in understanding structures, dynamics, and properties.

An important job of theory is to explain and predict phenomena. Two decades ago, we became interested in atoms and molecules under extreme conditions such as intense laser and strong magnetic fields. We pushed our time-dependent density equation into these difficult situations. With lasers, quite exciting results and insights were obtained into various multiphoton processes such as spatial shifting of density in both femtoseconds and attoseconds, photoionization spectra, high-order harmonics generation (its implication is the creation of attosecond and X-ray lasers), suppression of ionization under a superintense laser, Coulomb explosion in molecular dissociation, etc. The mechanism of shortening of bond length in a diatomic molecule under strong magnetic fields was also studied. We have predicted that, if an oscillating strong magnetic field of an appropriate frequency interacts with a hydrogen atom, coherent radiation should be emitted. This remains to be experimentally verified. We have also proposed a new dynamical signature of quantum chaos and demonstrated it with strong magnetic fields.

We now come to excited states. Using a hybrid wave function-density approach and an interpretation of exchange proposed by other workers, we have been able to calculate excited state energies and densities of several hundred excited states of various atoms. These were singly, doubly, and triply excited states, autoionizing states, satellite states, etc., and involved both small and large energy differences.

- **You have worked mainly outside the boundaries of "chemistry." What are the interdisciplinary areas that you have worked on?**

  I do not think I have worked outside the boundaries of chemistry, which are actually limitless. An interdisciplinary research area that I have pursued is the quantum theory of structures, dynamics, and properties of atoms and molecules. I have had great pleasure in devoting some time over the years for designing exciting and colorful chemical experiments, based on research literature, for undergraduate and postgraduate teaching laboratories. Each of these brings as many sciences as possible on the common platform of one single experiment. This was to partly satisfy my hunger for experimental chemistry! Also, writing on integrated learning in sciences, designing new curricula and developing new courses have been something of a passion. I have had a life-long interest in science, mathematics, literature, and art in Ancient and Medieval India, on which I am writing a book for the last five years. The idea of holism of Ancient Indians that everything is connected to everything else has always fascinated me because this is the essence of multidisciplinarity.

- **What do you see as things that have changed in the field of chemistry, especially theoretical chemistry and computational chemistry?**

  I see considerable development in the interfaces between chemistry and biology, as well as between chemistry and materials science. Some

development has also occurred in the interface between chemistry and earth science, as well as between chemistry and archaeology (e.g., archaeometry). With the advent of improved computer hardware and software, the way chemistry used to be done has changed, in the way data are recorded and analyzed. Computational chemistry software are being used almost routinely by many experimental chemists. Computational chemists are themselves using standard software packages to tackle more and more exciting and challenging problems. Two- and three-dimensional visualizations (graphics) are increasingly being employed. Experimentally, attempts are being made to probe single molecules rather than molecules in an assembly. Combinatorial chemistry, as well as green chemistry, has been in existence for some time. A synthesis protocol using artificial intelligence also exists. Attosecond (10^{-18} s) phenomena, concerned with electronic motions, have emerged very recently. Overall, I sense a great churning taking place in chemistry.

- **What do you think lies in the future of theoretical chemistry and computational chemistry?**

  If I am not wrong, of the total global population of theoretical and computational chemists, 90% or even more are computational chemists. Two things ought to be noted here. Software packages represent the technology of theoretical chemistry, and they employ existing theories which cannot be regarded as "perfect." Everybody knows that "all exact sciences are dominated by approximations." Chemical systems being highly complex, it would be rather unrealistic to play with toy models which admit analytical solutions. Therefore, the need for developing new concepts for improving existing theories would remain strong because this is an open-ended quest. Needless to say, software packages should not be used as "black boxes."

  I have a feeling that the number of theoretical chemists who can traverse the whole gamut of theoretical chemistry, *viz.*, generation of concepts, formalisms, algorithms, computer codes, and new ways of interpreting computed numbers, is decreasing steadily all over the world. Urgent replenishments are needed through the induction of bright, imaginative, and capable young chemists. In a way, theoretical chemists are akin to poets, admittedly with a practical bent of mind. We need to ensure that poetry, imagination, and the fun of making predictions do not disappear from chemistry.

- **Where do you think physical chemistry stands relative to other areas like inorganic and organic chemistry? (in terms of number of researchers, publications, Nobel Prizes, etc.)**

  Since my undergraduate days, I have been acutely uncomfortable with the attitude that chemistry can be completely classified into inorganic, organic, and physical chemistry. These are artificial intellectual barriers. The numbers of researchers and publications in certain areas of chemistry have been steadily increasing and will continue to do so. In terms of the number of researchers in various areas, there has been a seriously lopsided development in some countries because of the tripartite classification. One

even hears of cases where there is a large number of Ph.D. students with just one Supervisor. I hope the situation will improve and a balanced development will take place. Until 1960s, successive Nobel Committees apparently did not find theoretical chemists worthy of the Nobel Prize, although the latter had enormous impact on the whole of chemistry. That also changed from the 1960s. Of late, even a theoretical condensed matter physicist has received the Nobel Prize in chemistry. So, the earlier we teach ourselves to climb over these barriers, the better for the growth of chemistry.

- **How are Physical Chemistry and Chemical Physics different from each other?**

  Since both the terms refer to the interface between chemistry and physics, they should have the same meaning. However, in usage, this is not so. The term "chemical physics" was coined in the postquantum mechanical era and popularized by journals in chemical physics. One might simplistically say that, if, in the chemistry–physics interface, one is veering more toward chemistry, then one is doing physical chemistry, whereas, if one veers more toward physics, one is doing chemical physics. Alternatively, since science develops by progressive quantification, one might say that chemical physics is the modern more quantified version of physical chemistry. But I think all such distinctions are somewhat contrived. However, chemical physics has certainly been enriched by contributions from many physicists who probably felt more comfortable with this term than "physical chemistry." It may be worth noting here that an "overzealous" scientist had once defined physical chemistry as "the study of everything that is interesting"!

- **How has computation changed the way research in chemistry is carried out?**

  Over the years, there has been a sea of change in the attitude of chemists. Earlier, any theoretical method and the numbers computed from it had to be justified by comparing with experimental results. This has drastically changed because of two reasons: First, the sophistication in theory, algorithms, and computer codes is now so good that these frequently deliver computed numbers much beyond present-day experimental accuracy. Second, there are many situations in which it is extremely difficult to perform an experiment, e.g., to study a very short-lived molecule or study a phenomenon like the folding of a protein in a biological environment. Theoretical and computational chemistry could be the only route to take in such cases.

  Let me give you an example of accuracy of a theoretical method. In the last five years, it has been possible to numerically solve the Schrödinger equation for some systems with a precision of forty significant figures! While I do not understand the experimental significance of numbers beyond a certain significant figure or what we can do with such precise numbers, the fact remains that such computational accuracy is now deliverable and it challenges experiment. This is definitely good for overall development. Another recent development is the experimental tomographical picture of the highest occupied molecular orbital of the N_2 molecule, which proved the physical existence of a wave function.

With the availability of dependable and commercially available software packages developed by theoretical and computational chemists, in collaboration with experts in numerical methods, an interesting situation has come about. The synthesis and structure of a new molecule discovered in the chemical laboratory is nowadays justified by experimentalists by doing a geometry optimization according to a good software package. On the other hand, the experimental determination of structure generally resorts to a combination of methods.

However, we should never forget that experiment and theory are the two wings of a bird named science. It cannot fly on only one wing.

- **On one hand, the boundaries between chemistry and other sciences are blurring, and on the other, chemistry is branching out into specialized courses/fields. How do you think this is making a difference? Is the effect getting balanced out in some way?**

I look at it differently, instead of a balance or an imbalance. I like to spell "Chemistry" as "Chemistree." The Tree of Chemistry is large. It has deep roots and spreads in all directions. It has many branches and subbranches. New branches, subbranches, and leaves sprout in the course of time. As chemists, we are like birds living on this tree. A group of birds might nest in a small subbranch. There is no harm in that as long as the birds leave their nest once in a while and become aware of the large tree.

I believe there is a network of sciences, humanities, and social sciences with chemistry as a central science. I think future teaching and research in chemistry might develop along such a network.

- **What significance did the International Year of Chemistry (2011) have for you? What would you like to see changing in the future about research in chemistry?**

Let me answer the first question first. Chemistry has always been a deeply humanistic subject. For six thousand years, chemistry has worked for the benefit of humankind. Therefore, IYC did not remind me anew of chemistry in the service of humankind. Instead, it reminded me of two individuals whom I greatly admire: Madame Marie Sklodowska Curie and Acharya (Sir) Prafulla Chandra Rây. Besides being the centenary of Madame Curie's Nobel Prize in chemistry, 2011 was also the 150th birth anniversary of Acharya Rây, the first modern chemist of India and, along with Acharya (Sir) J. C. Bose, the founder of modern scientific research in India. As a teacher, Acharya Rây had inspired Meghnad Saha (the founder of modern astrophysics), Satyendra Nath Bose (the founder of quantum statistics), Jnan Chandra Ghosh (pre-Debye–Hückel theory of strong electrolytes), and many others. Besides his own well-known researches in chemistry, he was the founder of the chemical and pharmaceutical industries in India and an indefatigable social reformer. He was one of the greatest sons and builders of modern India, greatly admired by Mahatma Gandhi and Rabindranath Tagore, as well as numerous other persons, because of his asceticism, scientific modernism, deep knowledge about classical Indian culture, and a life totally dedicated to others.

There are striking parallels in the lives of Madame Curie and Acharya Rây which set guidelines for other human beings: poverty, suffering, indomitable spirit which does not recognize any obstacle, pioneering works in spite of continued ill health, tremendous leadership, building of multiple institutions, as well as an ascetic life totally devoid of self and completely dedicated to the welfare of others.

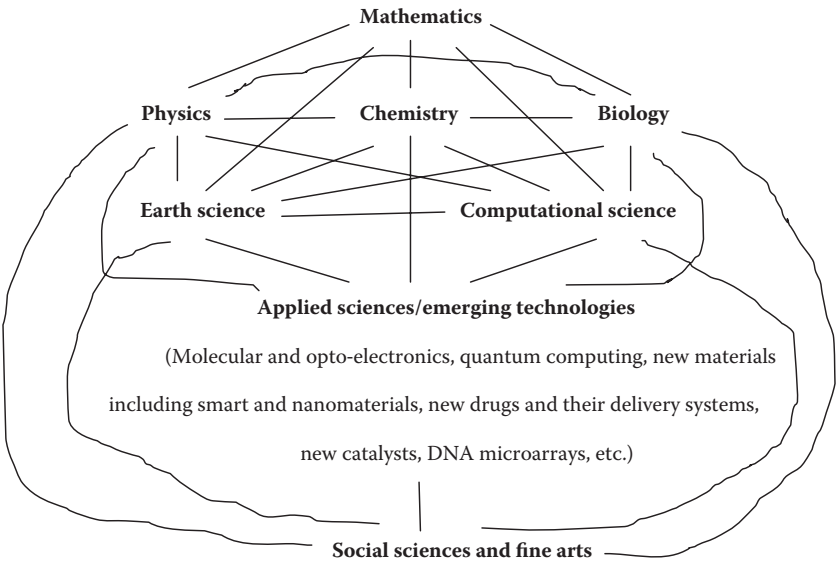
Coming to the second question. Within the global scenario, I believe we are not too bad in dealing with problems of fundamental importance in chemistry. However, I would like to see much greater intensity here, in terms of issues which were not tackled before. Where I would like to see extensive leapfrogging is in the development of new and sophisticated technologies born in chemical research laboratories, in collaboration with other scientists and engineers, wherever necessary. Some examples would be attosecond and X-ray lasers, a working quantum computer, new drug molecules by drastically cutting down the laboratory-to-market time schedule through a clever but absolutely safe multidisciplinary approach, etc. The list is actually quite long. Increasingly sophisticated chemical technologies which would be inexpensive and eco-friendly and can improve the lives of common people, especially those in rural and impoverished areas all over the world, need to be developed as quickly as possible.

- **You were involved in the development of chemistry curriculum for Indian universities. What are the key aspects of a good chemistry curriculum according to you?**

  A curriculum involves a combination of teaching, learning, and assessment. Irrespective of what an individual chemist may practice in his/her own research, a chemistry curriculum must not split chemistry into inorganic, organic, and physical chemistry, and there should be no specialization in any of these three up to the graduation level (pre-Ph.D.). I strongly believe that this tripartite splitting has done enormous damage to the free development of chemistry in certain countries. Throughout the undergraduate years, there should be self-exploration by the student through as many small and medium projects as possible. Science can be learnt only through a dialog with Nature, through experiments in the laboratory, and in natural environments outside the laboratory. Laboratory programs in certain countries are not in a good state. We must bring back imagination, excitement, and wonder into the laboratory courses in chemistry. This is easier said than done. Here, theoretical and computational chemists should join hands with their experimental colleagues in devising concept-oriented, technique-intensive, and generally fun experiments for students. We must also bring back experimental demonstrations during classroom lectures. Let us not forget that chemistry is a subject combining magic, logic, and aesthetics.

  The life-blood of any educational program is a dedicated and conscientious band of teachers. I would request the teachers concerned that, in formulating any chemistry curriculum, they should keep in mind that chemistry is a *central science*, overlapping with practically any subject under the sun and even the processes occurring in the sun, in the earth, and

elsewhere. Here, I would like to draw a connectivity network which depicts chemistry as a central science, and teachers as well as students may keep this in mind. Note that seven lines, some of which are coincident, radiate out from every subject toward other subjects. Both teaching and research in chemistry might develop in the future along this network.



Within this pattern, a chemistry curriculum must impart both *intellectual and manual skills* to the student and try to *integrate both skills*. This is the essence of creativity.

- **What kind of prospects do young theoretical and computational chemists have?**

  I strongly feel that every chemistry department in colleges and universities should appoint at least one theoretical and computational chemist. In universities, the critical number would be three. Because of the multidisciplinary nature of the subject, a theoretical chemist can teach quite a few areas and would therefore lend strength to the teaching programs. Secondly, industries in a number of countries do not seem to have felt the need to appoint theoretical and computational chemists. All these have drastically reduced the employability of young theoretical and computational chemists, who show enormous personal courage to go into these areas. As a result, theoretical and computational chemists have found employment only in a limited number of institutions. I find this overall situation fraught with danger for the future development of chemistry.

- **What sparked your interest in Chemistry? (You had done a Ph.D. in mathematics.)**

  I drifted into chemistry. I could see myself also in literature or medicine or biology or physics. However, even though my father was a legendary

teacher of mathematics, I never saw myself as a mathematician. An encounter with a highly charismatic teacher of chemistry put me into chemistry at Presidency College, Kolkata. I began to love the subject because of its all-encompassing nature. I was seriously thinking about going into experimental chemistry. It was a distinguished polymer chemist who advised me to pursue my doctoral studies with Professor C. A. Coulson. Since Professor Coulson was the Director of the Mathematical Institute of Oxford University, my D.Phil. degree was under the Mathematics Faculty at Oxford. Still, it took me six months at Oxford to firmly conclude that theoretical chemistry with its unlimited expanse will be my life, mainly because I knew that I would never be able to come to grips with it.

Looking back, I am convinced that it was my teachers right from high school to the doctoral level who were instrumental in charting my professional life.

- **Is there a particular incident from your research career, an anecdote, that you would like to share with the readers?**

  I recall an incident which helped to redefine the course of my research. Around 1970, I had written an article on what I called "the force concept in chemistry" for students and teachers of chemistry. The chemistry journals I sent it to declined to consider it for publication, saying this would be beyond their readership. Exasperated, I sent it to Professor Coulson for his critical comments. Professor Coulson decided to communicate it himself to Reviews of Modern Physics (RMP). It was highly interesting that, while the referee(s) accepted the article, Professor U. Fano, the Editor of RMP, wanted me to rewrite parts of it, making an extremely important point that I comment on how the electron density can be calculated directly. I wrote whatever I could, and the article was published. I was rather unnerved but elated when I received many letters from people belonging to various disciplines, including several highly respected scientists. One of them was Professor R. P. Feynman who, besides telling me that he liked the article, suggested that I look into stresses in molecules, which he himself was interested in at one time but never published anything on it. Enclosed with his letter came the Xerox copies of relevant pages on stresses from his B.S. dissertation (under J. C. Slater) at MIT, which contained his famous work on the Hellmann–Feynman theorem. These two suggestions changed my research.