

BOOK REVIEWS

Annual Review of Physical Chemistry, 2018. Mark A. Johnson and Todd J. Martínez (eds). Annual Reviews, 4139 El Camino Way, P. O. Box 10139, Palo Alto, California 94303-0139, USA. Vol. 69. vi + 557 pages. Price: US\$ 112.

I was excited when I was asked to review this volume of the *Annual Review of Physical Chemistry (ARPC)* because I could read the articles by active practitioners on current topics in physical chemistry. With the growing literature, one could no longer pretend to be up on things even in one's own domain of science. *ARPC* gives you the pulse of physical chemistry as it is practised, covering a wide spectrum (pun intended), from molecules to materials, living as well as non-living. The approach could be *ab-initio* or phenomenological, bottom-up or top-down.

One thing I love about each issue of *ARPC* is the prefatory chapter that provides a scientific 'autobiography' of a well-known physical chemist. It gives a glimpse into the evolution of the career of the 'physical chemist of the year', if I may say so, and how his (Marilyn Jacox was a single woman to write the prefatory chapter in all 69 years of existence of *ARPC*, as far as I could tell) area of research has evolved over the years. For the first decade or so, the prefatory chapter was invariably on thermochemistry and thermodynamic properties of substances. An exception was the chapter by Coulson. In subsequent years, it was on subjects such as physical organic chemistry and the history of physical chemistry in different institutions and different countries. Post 1975, the focus has been on individuals (with some exceptions).

Be that as it may, this year's subject is one of my heroes, Rafeay Levine. I tried to learn scattering theory from his book, *Quantum Mechanics of Molecular Rate Processes*. I realized later that it was distilled wisdom of a young and upcoming theoretical chemist, not meant for the uninitiated. Sure enough, the book has become a classic, reprinted by Dover. A classic, by definition, is a book that everybody talks about, but seldom reads. I was more than adequately compensated when I read Levine's book, *Molecular Reaction Dynamics*, co-authored by R. B. Bernstein. It is definitely a candidate for Kindle for the young generation.

It is difficult to summarize Levine's contribution to the area of chemical dynamics. Together with Bernstein, he wrote many papers on information theoretic approach to chemical dynamics. Their work was a forerunner to dealing with big data. Information theoretic analysis and synthesis were keywords for nearly a decade. I was definitely influenced by them. The only paper I wrote on the subject was, not surprisingly, co-authored with Levine.

My generation was not sure if it was possible, even in principle, to record the spectrum of the transition state of a chemical reaction. When Ahmed Zewail's work on femtochemistry evolved, many of us thought that it was the end of the road for temporal resolution in chemical dynamics. Levine has clearly shown that there is a lot of chemistry to learn by studying attosecond physics. It is no longer confined to the ground state; it involves several electronic states; one has to go beyond Born–Oppenheimer approximation. This view is reinforced by the review by Schuurman and Stolow, pointing out the role of conical intersections in excited state chemistry and the importance of time-resolved photoelectron spectroscopy (TRPES). The value of studying slow photoelectron velocity-map imaging (SEVI) of cryogenically cooled anions to unravel the structure of the neutral species and to determine the structure of different transients in a chemical reaction is emphasized by Weichman and Neumark.

When I started reading the rest of the articles in this volume, I was richly rewarded. On the one hand, the fundamental problems continue to be solved more and more accurately for small systems, while knowledge continues to accumulate for larger and larger systems, albeit at a phenomenological level.

Varandas shows how one could extract the 'exact' potential energy information in the complete basis set limit for small molecules. Once the potential energy surface for an elementary chemical reaction is generated as a function of various coordinates involved by highly accurate *ab-initio* calculations, the problem of fitting it remains a challenge. My own Ph D thesis showed the way by using cubic splines; but the approach remained directly applicable to systems involving up to three degrees of freedom (only). However, the efforts to represent potential energy surfaces for chemical reac-

tions involving several atoms continued, particularly using permutationally invariant polynomials. One must read the chapter by Bowman and co-authors to appreciate the effort involved in fitting potential energy surfaces for 'large' (up to 10 atoms) systems. This is not to be confused with the developments in force-field calculations, which are excellent for studying conformational changes in as big a molecule as one desires, as long as bonds do not break or form. When bonds break, the method breaks down. Various efforts have been made to combine the strength of molecular mechanics with the accuracy of quantum mechanical methods over the years. Computing potential energy and its derivatives as a function of coordinates on the fly in a trajectory has been one option. Using machine learning to solve the problem of fitting potential energy surfaces for large systems is an option that is likely to bear fruits in near future. Wales writes about multidimensional potential energy landscapes with multiple minima. Choi *et al.* illustrate the use of graph theory for ion and molecular aggregation.

Many researchers regard that the days of physical chemistry are over. They consider that physical chemistry is all about materials science, making of new materials, characterizing them and exploiting their properties for energy conversion and energy storage. They could be used as sensors too. Nature has been doing it all along. Therefore, it is all about biomimetic, bioinspired and bio-mediated materials. The chapter by Yaraghi and Kisailus on nacre structure formation is highly informative, providing an insight into how nature builds beautiful shells with interesting patterns, layer by layer. The fun lies in mimicking it in the laboratory. It requires enormous efforts and sophisticated tools to do what nature does 'routinely'.

There has been a lot of excitement in the last two decades on the study of soft matter. The self-assembly of molecules, nucleation and the resulting architecture have indeed been fascinating. Pattern formation in nature has its origin in diffusion and self-assembly. Mallory *et al.* describe recent advances in understanding colloidal self-assembly and its utility.

One can learn the basic principles of physical chemistry and apply them to larger and larger systems in a bottom-up approach. This is easier said than done. As mentioned earlier, the bottom up

approach may not work in many cases. One could go top-down too. So, one could start with condensed matter physics of materials. Alas, the twain never meet.

The classic case is that of metallic clusters. One could study them *ab initio*, starting from a single atom and moving on to multi-atomic clusters. One has to necessarily abandon the *ab-initio* approach at some stage and adopt a density functional theoretic approach as one climbs up the ladder. One had to ensure that the relativistic effects are taken care of, albeit in a semi-empirical manner. At one time, people believed in 'magic' numbers. That belief seems to have withered away. The question of when a metallic cluster becomes a metal remains.

The study of metallic clusters is not just to obtain knowledge. It has practical applications, particularly in the area of catalysis. While Weerawardene *et al.* illustrate how theory and experiment have worked hand-in-hand in determining the geometric and electronic structure of gold and silver nanoclusters, Jimenez-Izal and Alexandrova focus on the design of clusters for catalysis.

Chemistry is all about bond-breaking and/or bond-forming. Real-life chemistry involves complex systems. Not necessarily complex in terms of the size of the molecules involved, but in terms of spatio-temporal variations. When one wants to understand the molecular processes

underlying Alzheimer's disease, one needs to know not only how proteins fold, but also how they misfold and aggregate to form fibrils. That chemical kinetics is indispensable in linking the underlying mechanism and macroscopic measurements is brought out by Dobson and collaborators. In addition to giving an introduction to rate laws and amyloid fibril formation, they emphasize the role of master equation approach and coarse-grain modelling in the endeavour.

We used to consider that one- and two-dimensional (2D) models were key to understanding the real world, in three dimensions. However, today, with 2D materials becoming a reality, the need is to understand them at the 2D level, with their own interesting (new) physics. Sangwan and Hersam discuss electronic transport in 2D materials. Amori *et al.* discuss excitons in single-walled carbon nanotubes and their dynamics. Jonas deals with vibrational and nonadiabatic coherence in 2D (in a different sense of the word) electronic spectroscopy.

Rates of chemical reactions can be enhanced, traditionally, by heating or shining light or adding a catalyst. A combination of heat, light and catalysts can also be used. Guo *et al.* describe elementary chemical reactions in surface photocatalysis. Nogueira and González discuss computational photophysics in the presence of an environment.

Much of our effort in recent years has gone into understanding biological processes; to understand the underlying inter- and intramolecular interactions, the effect of electric and magnetic fields, self-assembly and transport across membranes. Slocum *et al.* discuss some of these aspects. Moringo *et al.* illustrate the utility of super-resolution microscopy.

Sensing chirality is essential in separating enantiomers. That rotational spectroscopy can be used for the purpose does not come as a surprise. However, it has been demonstrated only recently. Domingos *et al.* provide the details.

What distinguishes chemistry from alchemy is the knowledge of forces that underlie chemical processes and control them. If problems of today's world (air pollution, global warming, etc.) are attributed to chemistry, their solution lies in chemistry. If the level of carbon dioxide in the atmosphere is too high because of anthropogenic activities, fixation of carbon dioxide can also be achieved by us using chemical processes. Dodson *et al.* dwell on characterizing the intermediate oxidation states in CO₂ activation.

N. SATHYAMURTHY

*Jawaharlal Nehru Centre for Advanced
Scientific Research,
Bengaluru 560 064, India
e-mail: nsathyamurthy@gmail.com*