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Physical chemistry is a vast subject with ever-increasing radius of influence on other fields of study. Gone are the days when one could easily keep up with the forefronts of research by thumbing through a journal or two. In these times of superspeciality, there is a constant need for reviews from a broad perspective that communicate the current excitements in physical chemistry. *The Annual Reviews of Physical Chemistry* (*ARPC*) does just that: bite-sized morsels of the latest and the coolest in the field. This volume has 31 articles spanning nearly 800 pages. In contrast, vol. 60, which I had the pleasure of reviewing earlier, had 24 articles spread over 500 pages. Perhaps a sign of the ever-expanding frontiers of physical chemistry? Or is it time for making *ARPC* biennial? Interestingly, for the last couple of years, *ARPC* does not have its customary editorial preface – hopefully, this justifies the need for the present review.

The volume begins with the prefatory chapter, usually a biographical memoir of an outstanding physical chemist, in this case James T. (Casey) Hynes. Having met Casey a few times, most recently in 2014 when he visited IIT Kanpur, I read this chapter with avid interest. One can clearly see his unique way of putting things across to the reader. This account of his group's efforts to understand the molecular dance in gas and condensed phases, all the while 'thinking like a molecule', clearly reflects the intensity and passion that Casey brings to the field of theoretical chemistry. For example, towards the end of the section on vibrational energy flow he gives a vivid description of the energy flow dynamics in hydrogen peroxide. And then there is the honest admission – 'To my regret, we never succeeded in capturing/understanding this in a nonlinear resonance framework'. Taking us through a rather broad range of problems, Casey manages to convey an important message that 2 : 1 Fermi resonances and proton relay chains are ubiquitous in chemical reaction dynamics.

Chemistry at surfaces/interfaces is an area of considerable activity in the recent years and thus, not surprisingly, four chapters highlight various developments in this field. The first one by Ilan Benjamin gives an account of the advances in theoretical and experimental understanding of reactions at liquid interfaces. Nucleophilic S_N2 reactions have become the focus of gas phase as well as condensed phase studies. Benjamin highlights the role of interfacial structure on phase transfer catalysis of a S_N2 reaction across a liquid–liquid interface. Interestingly, a charged solute seems to be able to keep the hydration shell as it goes across the water–chloroform interface. This is followed, appropriately, by an article by Wang *et al*., wherein the recent developments in the technique of sum-frequency generation vibrational spectroscopy are discussed. The authors bring out the subtle aspects of this technique in a clean manner and provide enough details so as to be useful for a graduate student in the field. The third article on surface chemistry by Alec Wodtke and co-workers is concerned with molecular reaction dynamics on metal surfaces. Personally, I think that this review is brilliantly written and is an example of how one should write a critical review which compares and contrasts theory and experiments. The discussion starts with the so-called standard model of chemical reactivity and ends with the final comment on being destined to work with 'simple models that we know to be flawed'. This article should be mandatory reading for students, experimental or theoretical, who wish to enter this challenging field of research. Finally, a review by Wang *et al.* provides the current state-of-the-art in modelling photoinduced dynamics at nanoscale interfaces. The article highlights the power of time-dependent density functional theory and non-adiabatic molecular dynamics techniques in a variety of systems ranging from molecular crystals to nanoclusters. Table I in the article is a particularly informative summary of the existing methods and their limitations.

Reaction dynamics in gas and condensed phases are at the core of physical chemistry. Recent experiments are starting to 'point out when and where flaws are likely to occur in simple models' for reaction rates. The article by Kaiser *et al*. gives a succinct introduction to the mechanisms of formation of polycyclic aromatic hydrocarbons (PAHs) in interstellar medium. In addition to illustrating the utility of crossed molecular beam experiments (for instance, see figure 4 of the article), the authors make a case for the possibility of formation of the aromatic hydrocarbons at ultracold temperatures, as opposed to conventional arguments requiring high temperatures, via barrierless reactions. Kaiser *et al*. ascribe the delay in studying PAH prototypes via molecular beam techniques to the difficulties in generating stable supersonic beams with sufficiently high concentrations of the reactants. In this context, the article by Jankunas and Osterwalder summarizes the recent advances in the production of controlled cold molecular beams. Apart from providing a compact historical perspective, the article emphasizes the advantages of cold molecular beams in terms of extracting the detailed features of the potential energy surface. It is now possible to study phenomena like Penning ionization, tunnelling resonances, conformer-selective reactivity and rainbow scattering in great detail. Another direction involving studying reactions at cold temperatures requires exquisite control over collision process and geometry. Heazlewood and Softley review a technique, based on laser-cooled atomic ions in Coulomb crystals, that would allow one to understand the rates and mechanisms of ion–molecule reactions at very low energies. Quantum effects are expected to be pronounced at low temperatures and detailed studies may just provide interesting challenges to theorists. Clearly, exciting developments like Stark decelerator and cold atom traps are truly ushering in a new era in reaction dynamics.

Reaction dynamics and energy transfer are inseparable. In recent years, there has been an increased focus on transfer of electronic and vibrational energy in a variety of systems. The prefatory chapter already provides a glimpse of the intricate molecular dance in gas and solution phase that comes about due to the subtle interplay of intra- and intermolecular energy transfer processes. The spirit of the prefatory chapter is amplified further in a couple of articles that highlight the striking advances in our understanding of energy flow dynamics in complex systems. The review by Orr-Ewing on time-resolved infrared studies of bimolecular reaction dynamics in condensed phases is well written. The issue of how much of the insights from gas phase studies can be extended to the solution phase is

addressed using several examples. Surprisingly, the solvent only partially quenches the nascent vibrational energy in the reactants. It would seem that studies along these lines should go in parallel with recent theoretical work on transition state theory in condensed phases and noisy environments. Given the interest in unravelling the role of solvents at a 'gas phase' level of detail, it is not entirely surprising that several novel experimental techniques have been put forward. One such technique involves two-dimensional spectroscopy. The review by Rubtsova and Rubtsov provides an approach that uses the vibrational energy flow, often considered to be a necessary hindrance, as an advantage. The relaxation assisted two-dimensional infrared (RA 2DIR) technique involves exciting a specific tagged mode which, via vibrational energy flow, communicates with a reporter mode. Interestingly, the intramolecular energy flow overcomes the distance constraints in traditional two-dimensional IR and one observes ballistic, as opposed to diffusive, energy transport in long-chained molecules. It seems like controlling reactions in solutions by controlling energy flow should be feasible in the near future. Or is this another teaser akin to the gas phase case a few decades ago? Given that the tagged mode and the reporter mode get correlated by IVR, an intriguing possibility is to engineer specific modes to 'play' with the energy flow pathways and thus deconstruct the RA 2DIR information. So, how can one incorporate site-specific IR probes in complex systems? Answers can be found in the review by Ma *et al*., wherein several types of extrinsic IR probes are discussed. Starting with a discussion about what makes an ideal site-specific probe, Ma *et al*. make it clear that *avant-garde* IR spectroscopy is anything but a blackbox.

Electronic energy transfer processes, from Kasha's rule to Graham Fleming's observation of distinct energy pathways in light-harvesting complexes, continue to be the focus of study by physical chemists. More recently, apart from vibrations jumping into the fray, the role of quantum coherence in complex systems has fuelled heated debate in the community. In fact, one has to be cautious in interpreting something as due to a coherence effect. For instance, in a lucidly written perspective (*J. Chem. Phys*., 2012, **136**, 210901), Bill Miller concludes by saying that '...coherence effects may be of quantum or classical origin and that it is not always obvious which it is'. Nevertheless, a particularly clear account of coherence of energy transfer in photosynthetic systems is given by Chenu and Scholes. Little surprise then that they have a section titled 'How to think about coherence' – a must read for everyone. Chenu and Scholes give a careful presentation of the dynamics of light-harvesting systems and the regimes of energy transfer, where one can genuinely claim quantum coherence effects to be present. Again, it is two-dimensional electronic spectroscopy which is the key tool to gain insights into such complex systems. Quite appropriately, not sure if by design or sheer coincidence, a review by Fuller and Ogilvie gives the state-of-the-art in two-dimensional Fourier transform electronic spectroscopy. This article gives the experimental details with great clarity and also sums up the challenges faced while using the technique. For example, their figure 2 (illustrating the information content in a 2D spectrum) and table 1 (summarizing the experimental constraints and benefits/drawbacks of various implementations) seem to be a good starting point for anyone who is interested in jumping into this exciting arena of spectroscopy. The issue of quantum coherence also shows up in a fundamental many-electron process known as singlet fission. In this spin-conserving process, a photoexcited singlet state can generate two triplet excited states due to coupling between the chromophores on two molecules. Monahan and Zhu review the advances made in our understanding of the charge transfer-mediated singlet fission process. For strong electronic couplings, they argue for the importance of considering quantum coherence for an accurate estimation of the singlet fission rates. On a different note, but still dealing with electronic processes, Vöhringer's review of the ultrafast dynamics of ammoniated electrons highlights a problem that has been around for a century. The complexities inherent to the relaxation dynamics of metal–ammonia solutions is just being unravelled using ultrafast spectroscopic techniques. One gets an idea of the complexity when the author states that the photoelectron spectrum of liquid ammonia is yet to be published.

The interface between chemistry and materials science is essential for coming up with novel materials with real-world applications. In recent times, efforts have been directed more towards miniaturization. Here quantum effects become important and can give rise to rather novel properties. Theoretical models need to be more carefully constructed and the ever-increasing sophistication of the experiments poses a challenge to theoreticians. One field where chemistry, physics and engineering need to work closely is the area of spintronics – where both electron charge and spin are crucial to understanding the transport properties in materials. The review by Naaman and Waldeck provides a glimpse of the challenges when electrons transport through chiral molecules. A very readable and clear discussion of the chirality-induced spin selectivity effect is given with figures 1 and 2, highlighting the nontrivial effects that arise due to the coupling of linear momentum and spin of the electron. The review ends with an intriguing question – has nature perfected the art of spin-selective electron transfer in biological systems? If so, this would be one more reason for biology students to start taking quantum mechanics classes and physics students to take chemistry lessons more seriously. If nature is indeed that smart then how smart can we get in terms of designing materials that harness solar energy? Zhugayevych and Tretiak provide the answer in terms of what can be achieved in a class of materials known as organic photovoltaics. Specifically, they provide the various factors that go into determining the power conversion efficiency. The theoretical challenges involved are beautifully highlighted in terms of the nature of the electronic states, decoherence effects and non-adiabatic transitions. Their critical discussion of models like the Holstein–Peierls Hamiltonian, always keeping experimental constraints in focus, is presented with great care and detail. Apparently, there is no clear-cut answer yet to the maximum power conversion efficiency that one can attain for a device based on a specific molecule. One way of overcoming the efficiency limits of photovoltaics is to convert low-energy photons to high-energy ones, a process known as photon upconversion. Sun *et al*. discuss a promising class of rare earth naomaterials that can lead to efficient photon upconversion. While we are on the topic of miniaturization, let us not forget the carbon nanotubes. A lot of work has been done

on them since the groundbreaking work of Iijima in 1991. Having been around a while longer than spintronics and photovoltaics, one wonders as to what has been done or is capable with carbon nanotubes. Li and Pandey review the recent developments. The applications range from solar cells, electrocatalysis, nanoelectronics, to even a computer whose CPU is based entirely on carbon nanotubes.

In several, if not all, of the experiments on complex systems mentioned above, gaining theoretical insights inevitably requires the usage of density functional theory (DFT). Therefore, I am happy to see the critical review of DFT by Pribram-Jones *et al.* Their quirkily titled review 'DFT: A theory full of holes' is an absolute pleasure to read. This is a review that every user of DFT must read – there is ample humour (young chemist, unable to find permanent position, ending up selling parametrized functionals for food on the streets) and veiled warnings about excessive empiricism.

Several of the reviews mentioned above are concerned with controlled engineering of materials and processes using external fields and molecular 'mutations'. However, what if the systems are left to their natural accord? One provides an interesting 'initial condition' and then let the laws of statistical mechanics and kinetics do the rest. Can some interesting patterns emerge from such processes? Nature, of course, is infinitely creative in this context, focusing more on optimizing the functionality of a complex system. Several reviews in this volume bring out the nuances of self-assembly in a variety of systems. Whitelam and Jack provide a clear introduction to thinking about the dynamical pathways of self-assembly from statistical mechanical viewpoint. Their discussion of thermodynamic versus kinetic stability, and the importance of far-from-equilibrium pathways (see figure 4 in the article) is especially well-written. Perlmutter and Hagan go deeper into the specific subject of how virus assemble. In particular, they discuss the thermodynamics aspects of assembly of the protein shell, known as capsid, that encases the virus. However, there are challenges in terms of experimental confirmation for the proposed intermediates along a specific pathway. The competition between kinetics and thermodynamics is also brought out clearly in the context of crystal structure prediction by Thankur *et al*. The notion of polymorphism in crystals, with its consequent computational challenges to determine 'a crystal structure' as opposed to 'the crystal structure', highlights issues that are common to those that arise in other self-assembly stories. Morriss-Andrews and Shea bring out the computational challenges in the context of protein aggregation. Table 1 in their article nicely summarizes the various computational techniques to study how proteins self-assemble. Although there are impressive advances, the near-boundless complexity presented by the system means that we are yet to grasp the process of amyloid fibril formation at the required level of detail. As Lehn points out in his Nobel Prize lecture (*Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1304), 'the score of chemistry is not just to be played but to be composed'. Along that thought stream, the review by Zhang *et al.* talks about the directional assembly using Janus (in Greek mythology, Roman god with two faces) colloidal particles. Adding chemically interesting patches on colloidal spheres with some anisotropy can lead to non-trivial structures. The authors give several examples and conclude with the challenges in this approach. In another interesting review, Lane *et al*. discuss the challenges of the behaviour of nanoparticles *in vivo*. Here is an example for using smart design principles to utilize modified nanoparticles as drug delivery agents. This requires an intricate understanding of how the designed systems interact with cells and tissues under physiologically relevant conditions. Challenges abound, but it is clear that such efforts at directed self-assembly are perhaps an attempt to 'compose the score of chemistry' and not just 'play the score of chemistry'.

For a student of molecular scattering and reaction dynamics, topics like Feshbach and shape resonances, dissociative electron attachment, Auger decay, and intermolecular Coulomb decay seem to be in the realm of fundamental chemistry with not much of an application in real life. Nothing could not be farther from the truth! In fact, the combination of ultrafast spectroscopy and insights gained into the processes mentioned above from small-molecule studies is helping us in understanding the damage of DNA by low-energy electrons and also the possible repair mechanisms. The review by Alizadeh *et al.* nicely illustrates the role of transient negative ions, formed due to the attachment of electrons to DNA, in cellular damage. Even the water present in the cell is not immune to this and can lead to cellular damage. It is fascinating to read the manner in which the advances in spectroscopy are leading to a better understanding of the mechanism of cell death. The short-time dynamics of DNA after absorbing ultraviolet radiation is described in great detail by Schreier *et al*. The differences between single-stranded and double-stranded DNA are brought out quite clearly. One does not have the required level of understanding yet and the authors point out the need for better experiments and good theoretical models. At the same time Zhong, in a detailed review, shows how the combination of femtosecond spectroscopy and site-directed mutagenesis can yield insights into the way in which a certain class of photoenzymes can repair this radiation damage to DNA. It is fascinating that the entire enzymatic pathway, aided by several electron transfer events, can be mapped out in some detail (figure 7 of the article). There is an important lesson here – it is not easy to predict as to how and on what timescale does a specific experimental tool, designed originally to study fundamental physical and chemical processes, may aid in bettering human life. I am sure that femtosecond spectroscopists did not have photorepair of DNA as a system in mind while setting up their first experiments.

The area of biophysical chemistry is also well represented in this volume. Liu *et al.* provide a basic introduction to the influence of mechanical force on cells. Molecular force spectroscopy is an emerging field which provides insights into the breaking and forming of non-covalently formed bonds. The authors make a statement that all molecular bonds in biology have a finite bond lifetime. It is a bit of a puzzling statement. Sure, non-covalent interactions dominate biological systems, but that does not imply that the chemistry of covalently bound units is irrelevant to biological systems. Nevertheless, assuming that the focus is on non-covalent contacts only, the authors introduce the notion of a slip, catch and ideal bond. Several novel examples like bacteria–host interaction and

cytoskeletal dynamics indicate that the field of mechanochemistry and mechanobiology are bound to provide tough challenges for theoreticians. Mehmood *et al.* provide a glimpse of the challenges involved in mass spectrometric analysis of protein complexes. In this context it is worth pointing out a recent text (Ghosh, P. K., *Introduction to Protein Mass Spectrometry*, Academic Press, 2016) that provides comprehensive information on the state-of-the-art in the field. The method of collision-induced unfolding is interesting, and it is clear that analysing the unfolding plots is a problem in dynamics that perhaps involves a central role for energy flow pathways in the complex.

In summary, this volume of *ARPC* shows the amazing breadth of physical chemistry. Indeed, it would take a certain amount of patience to go through it all and discover the connections between seemingly unrelated topics. Hopefully, this review has managed to group them in some 'coarse-grained' fashion and hence act as a guide for those who want to read up on the frontiers of a certain corner of physical chemistry. If you are short on time, then read the summary boxes provided at the end of most chapters. However, there is no substitute for reading the review in full. For active researchers, the reviews in this volume are perfect as a reference to the current level of understanding and the grand challenges that remain. Perhaps *ARPC* can make the summary box and an additional open questions box mandatory for every article.

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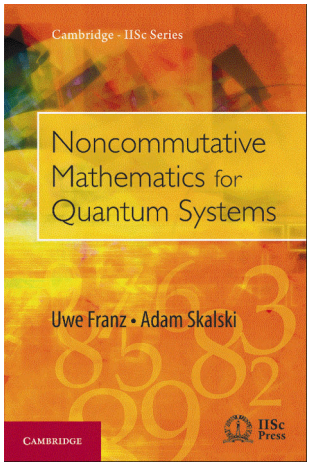

Noncommutative Mathematics for Quantum Systems. Uwe Franz and Adam Skalski. Cambridge–IISc Series, Cambridge University Press, 4843/24, 2nd Floor, Ansari Road, Daryaganj, Delhi 110 002, 2016. 125 pages. Price: Rs 950.

This monograph is based on lectures given by these two young mathematicians at an international workshop-cum-conference held at the Indian Statistical Institute, Bengaluru during 31 December 2012–11 January 2013. The authors are two of the topmost researchers and finest expositors of the subject of non-commutative mathematics. They give a friendly introduction to some recent developments in the field. Currently, there are no books covering some of the topics explained here.

This book is on quantum probability and to explain it we need to begin with classical probability. Consider one of the simplest of random experiments, namely throwing of a die. The outcome could be any number from 1 to 6. Actually if we know all the related physical parameters such as shape and weight distribution of the die, the force applied and the way it is applied and so on, at least in principle, it should be possible to predict the outcome accurately. However, in practice it is a rather difficult thing to do, as the number of parameters involved is too many and the mathematical equations coming from physical laws are too complex. In practice, we may believe that the die is a fair one and model the experiment using a triple $(\Omega, \mathcal{F}, P)$ as follows. The set of all possible outcomes, or sample space, is a set $\Omega = \{1, 2, 3, \ldots, 6\}$. Similarly $\mathcal{F}$ consists of events which are subsets of Ω, for instance, the set of odd numbers here, $A = \{1, 3, 5\}$ is an event. Then we assign probabilities to events, following certain natural rules. If we believe that the die is a fair one, it is natural to assign probability of A as three out of six, that is 1/2. Mathematically we write it as

$$P(A) = 1/2.$$

Starting with this elementary idea, and some combinatorics, we can answer questions such as what is the chance that we get eight successive 'sixes' if we throw the die say 1000 times. Here we are making use of probability theory. This model was originally proposed by A. N. Kolmogorov. It uses Boolean logic of a family of subsets of the set of all possible outcomes. These subsets are called events and probabilities are assigned to events. Here the machinery of measure theory comes in handy. The whole of probability theory is built with this model and it is the accepted model used in modelling all the 'randomness' we see in our daily life. We call this as 'classical probability'.

One of the major surprises of quantum theory is that it is non-deterministic. It has 'randomness' in-built in it. Even more surprisingly, Kolmogorov's model is not applicable here. One uses the logic of subspaces of Hilbert spaces and this probability theory has come to be known as 'quantum probability' or 'noncommutative probability'. It is the model applicable to quantum mechanics, and consequently indispensable for quantum computation, quantum information and other related fields. The phenomenon of non-commutativity appears here in a crucial way with serious mathematical and physical consequences.

The idea of having non-commutative or 'quantum' versions has spread to other areas of mathematics and has become a major trend of modern mathematics. At a basic level we have the theory of C*-algebras and von Neumann algebras as non-commutative topology and non-commutative measure theory respectively. At a much more sophisticated level we have non-commutative geometry and quantum groups. I quote the following paragraph from this book to explain the basic mathematical scheme followed for building these theories:

'The general pattern of the noncommutative mathematics is the following: take a "classical" mathematical theory, say topology, measure theory, differential