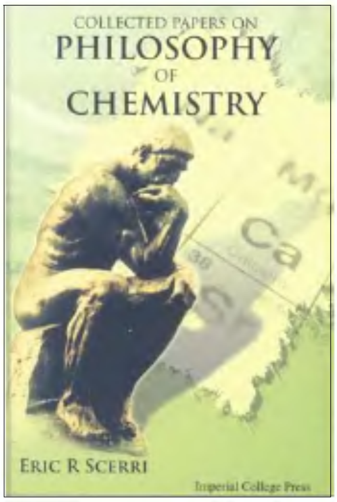

Collected Papers on Philosophy of Chemistry. Eric R. Scerri. Imperial College Press, 57 Shelton Street, Covent Garden, London WC2H9HE. 2008. 235 pp. Price not mentioned.

Philosophy of chemistry – at first sounds like a poor cousin to its more illustrious avatars in physics and biology. Every subject has its share of rich, sometimes dark, history and chemistry is no exception. However, philosophy of a subject is quite another matter. As opposed to history wherein one attempts to give a chronologically accurate account of the development of the subject, philosophy deals with issues of existence, need and the unique identity of the field. In this regard, physics and biology have had it made – one deals with origins of the universe and the forces shaping it, whereas the other deals with the origins of life itself. After all we humans have over the centuries grown up wondering about the heavens above and the complexity of the human brain that lets us comprehend the laws of the motion of the heavenly bodies. But where does chemistry fit in? Is there a need for a philosophy of chemistry? Is not chemistry, in the grand scheme of things, a 'middle kingdom', a 'third-party' mediator between biology and physics? This book takes such questions head-on and makes the case for the uniqueness of chemistry and its special place in the grand scheme of things.

I have unabashedly borrowed the expression 'middle kingdom' from Desiraju's enlightening article (*Curr. Sci.*, 2005, **88**, 374–380) that I had read a few years ago. Indeed, Desiraju quotes from the philosopher Kant at the start of his article:

> '. . . so chemistry can be no more than a systematic art or experimental teachings, indeed never real science, because its principles . . . do not lend themselves to the application of mathematics.'

One can pardon Kant since he could not have imagined the field of theoretical chemistry in 1786 (some even today wonder about the existence of this branch of chemistry. But that is another story!). So we do now have fundamental concepts like reaction rates, dynamics and their control amenable to the full glory of mathematics. For example, see the article by Trinajstć and Gutman (*Croata Chem. Acta*, 2002, **75**, 329) on 'mathematical chemistry' to appreciate the role of mathematics in the chemical sciences. Chemistry, therefore, is a very real science. But, is that not really theoretical physics in different clothes? If so, then chemistry being real science in the Kantian sense is of little comfort for most chemists. This is where Desiraju's article makes the case for chemistry indeed being THE middle kingdom with its own unique identity and philosophy. The various articles of Scerri emphasize the same point of view. At the heart of it all is the contentious issue of the reductionist viewpoint – can chemistry be reduced to physics? Being a theoretical chemist myself, I have had opportunities to ask this, perhaps uncomfortable, question myself with no clear answers forthcoming even now. So, I was quite excited to get this opportunity to read through Scerri's collected articles and draw a clear boundary (should one be drawing such boundaries?) between mathematics, physics and chemistry. However, before dwelving into Scerri's book I quote from the Nobel Prize address (*Rev. Mod. Phys.*, 1999, **71**, 863) by Laughlin:

> 'One of my favorite times in the academic year occurs in the early spring when I give my class of extremely bright graduate students, who have mastered quantum mechanics but are otherwise unsuspecting and innocent, a take-home exam in which they are asked to deduce superfluidity from first principles. There is no doubt a special place in hell being reserved for me at this very moment for this mean trick, for the task is impossible. Superfluidity, like the fractional quantum Hall effect, is an emergent phenomenon . . . The world is full of things for which one's understanding, i.e. one's ability to predict what will happen in an experiment is degraded by taking the system apart . . .'.

Contrast the above with Weinberg's notion of grand (as opposed to petty) reductionism (*Sci. Am.*, 1974):

> 'One of the enduring hopes has been to find a few simple general laws that would explain why nature with all its seeming complexity and variety is the way it is. At the present moment the closest we can come to a unified view of nature is a description in terms of elementary particles and their mutual interactions.'

Clearly, physicists have been having their own reductionist versus emergence wars to fight (see for example, Morrison, M., *Philos. Sci.*, 2006, **73**, 876). The last bit of the above statement by Weinberg has led to considerable acrimony within the physics community, but I will not say anything more about it since I am not qualified to do so. Nevertheless, a recent book edited by Bedeau and Humphreys (*Emergence*, MIT Press, 2008) promises to be an interesting read. Surprisingly, and sadly as well, there is no chemistry representation in this volume's contributors list. Thus, in a way it is quite appropriate that Scerri's collected articles was also published in 2008.

The emergent viewpoint is the basis for Desiraju's and Scerri's arguments – the periodic table, non-covalent interactions and hydrogen bonds being the prime examples to set the stage for a unique identity and philosophy of chemistry. For instance, Scerri argues that Bohr's 'prediction' of the nature of the element hafnium was somewhat ad hoc as opposed to being truly *ab initio*. At best it is an example of a weak prediction. Personally, I feel that Scerri is being a little too restrictive in his judgement of Bohr. Given that we are talking about a true multibody interacting problem and the fact that Bohr was trying to make sense of things using the old quantum theory, one is stretching things a little too far in criticizing Bohr for not being strictly deductive. A little later, in another article, Scerri asks if the periodic table has been successfully axiomatized. The answer is NO. In particular, there still does not exist a clear explanation for pattern 2, 8, 8, 18, 18,... of the period lengths as opposed to the $2n^2$ rule, which stipulates that any period can only have 2, 8, 18, 32,... for their lengths. The key point here is that the $2n^2$ rule can be explained/deduced from quantum mechanics, but 'explaining' the pattern of the lengths requires experimental inputs. Interestingly, as Scerri emphasizes in several places in the book, this point is not brought out clearly enough in most textbooks, modern or otherwise. One notable exception is the famous *Atomic Physics* book of Max Born! The other more recent example is Silfvast's book *Laser Fundamentals*, wherein he states that 'the actual shell-filling sequence has not been worked out in any systematic manner but has been determined primarily from spectroscopic evidence'. So, are the exceptional electronic configurations of niobium and chromium, among others, an example of emergent behaviour? Perhaps. Is it an example of the failure of the reductionist viewpoint? Maybe. However, I do like the refreshing take that Scerri has on this – as a challenge to theoretical chemists and physicists and to serve as a reminder of a feature that is not yet fully explained from quantum mechanics. This viewpoint is much better than in some forums wherein the discussion pretty much degenerates into petty reductionism versus petty emergentism. Interestingly, in contrast to Scerri's view, Desiraju considers the periodic table of Mendeleev to be the 'high noon of reductionism'.

Two other articles in the book entitled as 'Has chemistry been at least approximately reduced to quantum mechanics?' and 'Just how *ab initio* is *ab initio* quantum chemistry?' are fairly well-written. The main focus is on electronic structure theories and their capability to predict without the advantage of knowing the experimental facts beforehand. I found the latter article very well-written, barring an interesting reference to Dudley Herschbach as the 'theoretical chemist Herschbach', and needs to be made mandatory reading in any graduate-level structure-bonding course. This is particularly so that the students do not go away, at the end of the course, with a feeling that quantum mechanics predicts everything satisfactorily. However, the statements by Scerri in the context of figure 2, wherein the experimental and theoretical values of the first ionization energies of atoms are compared, are puzzling to me. The objection, which renders the theoretical prediction semi-empirical according to Scerri, has to do with the fact that the Schrödinger equations need to be solved atom-by-atom as opposed to a 'general solution' to the problem of electronic structure of atoms. First, even Mendeleev needed as many separate experiments to come up with his periodic table. So, what is wrong with an equal number of theoretical calculations? Secondly, I fail to grasp the meaning of Scerri's call for a general solution to the atomic Schrödinger equation – there is none! More than a century ago Poincaré had already showed the nonintegrability of an interacting three-body system and hence one cannot write down a general solution of the Schrödinger equation even for the helium atom. One is forced, therefore, to adopt a numerical approach. Note that even the inspired guess of Laughlin, now called as the Laughlin wavefunction, is not an exact eigenstate of the relevant Schrödinger equation in the general case.

Upon reading some of the other articles I get the feeling that Scerri is leaning towards adopting an intermediate position between reduction and emergence. I, perhaps being biased as a theoretical chemist, agree with this standpoint. It might seem like an easy way out, but the issues involved in taking a firm stand are subtle. For instance, are hydrogen-bonded systems and non-covalently bound systems truly the prime candidates for uncovering emergent behaviour? In that case what does one mean by defining a hydrogen bond? Why then are serious attempts being made, for example, by Hobza and co-workers, to accurately predict the properties of non-covalently bound systems using quantum mechanics? Could it be that in the far future we might be actually able to write down an expression for the 'hydrogen-bonding force' through a quantum mechanical derivation in analogy to the derivation of the van der Waals force? On a slightly different track, the 2010 Fields medalists Smirnov (proved that conformal invariance holds in the planar ising model) and Villani (obtained rigorous results for the rate at which an initial nonequilibrium distribution of gas particles relaxes to the long-time equilibrium Maxwell–Boltzmann distribution) have made groundbreaking contribution to two of the most fundamental and sought-after questions in physics. Smirnov's work is in the area of phase transitions, a supreme arena of emergence phenomena, and Villani's work is on the ultimate emergent phenomenon in physics – the arrow of time. Is this a victory for the reductionist or the emergent viewpoint? Does it matter? As it is, and should be, in science, the phenomena are beautiful facts of nature and an explanation of the phenomena is infinitely satisfying. Some of these sentiments are captured in the introductory chapter of Bedeau and Humphreys book – 'Hunting for emergence is an exciting sport, but the claim that something is emergent should be made with care and supported with persuasive evidence ... One should not lightly abandon nonemergent, reductionist approaches that have been successful in many areas of science and philosophy. At the same time, one should also note that many of the conceptions of emergence developed and defended in this book are consistent with many common forms of reductionisms.'

There are other articles in the book that bring out various philosophical aspects of chemistry with a special emphasis on the periodic table and the electronic structure and bonding in molecules. I also enjoyed reading his article on chemical education. In particular, Scerri urges departments everywhere to take the field of chemical education more seriously and says, rightly so, that chemical education is not simply about producing better visualizations and other multimedia gizmos. I am a bit disappointed that dynamics is completely left out of the discussions. Is it that there are no emergent structures in the dynamics of molecules? Perhaps it is too early to think about this issue. In any case, Scerri's collection of articles will keep the interested reader busy for a while. And, with some luck, might even motivate some of the younger, scientifically mature audience to contribute to the philosophy of THE middle kingdom.

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