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EDITORIAL

Editorial 37

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The latest edition contains a large variety of articles from many parts of the world including a rather special one from one of the giants in modern theoretical chemistry, Richard Bader from Canada. In his article Bader puts forward his views on chemical bonding as well as responding, in passing, to some of his critics. We are pleased that Professor Bader has chosen our journal to continue this interesting discussion. Let me take the opportunity of mentioning that a future special issue will be devoted entirely to the work of Richard Bader and will be edited by Cherif Matta, also working in Canada.

The next paper is from a newcomer to this journal, Eammon Healy, an Irish chemist based in Austin, Texas, who writes about resonance in chemistry from its introduction by Heisenberg up to the continuing rivalry between the molecular orbital and valence bond theories of bonding. The article is refreshingly technical and includes interesting historical asides from an author who has also recently published a piece on the foundations of quantum mechanics intended for a chemical audience.[1]

The Hungarian historian of chemistry Gabor Pallo is also concerned with the relationship of chemistry to quantum mechanics. His paper examines the work of two of his fellow countrymen, George von Hevesy and Michael Polanyi.

The fourth paper is by the Estonian philosopher of science, Rein Vihalemm who addresses the work of several authors working in the foundations of chemistry including Lombardi, Harré, van Brakel, myself and others. Vihalemm is critical of attempts to bring metaphysical considerations to the fore and argues for a position that he calls practical realism.

Rom Harré based both in the UK and the US, and Jean-Pierre Llored in France, write together about mereology in chemical discourse, that is to say part-whole relationships. The authors consider the relative virtues of Lesniewski's classical mereology as well as David Lewis' set theoretical approach to mereology. They do this in the context of the status of elements in compounds, atoms in molecules and atomic orbitals in molecules.

[1] Healy (2010).

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Two books are reviewed in this issue. The first is a concise review by Michael Laing from South Africa of a popular book on the elements that has been on many best-seller lists since it first appeared about a year ago. The book by Sam Kean has done a great deal to popularize knowledge of the elements and the periodic table among general readers. The publication of this, as well as a similar and more recent book by Hugh Aldersey-Williams, would finally seem to bring an end to the lack of good popularizers of chemistry.

The other book review is by the US chemist-philosopher Joseph Earley who analyzes an important book on atomism by Alan Chalmers. Briefly stated Earley objects to what he sees as Whiggism and a neglect of scientific developments involving the accommodation of data rather than strict prediction in Chalmers' book.

Some recent developments in the field

I would like to turn to the appearance of an article on the philosophy of chemistry that has been long in the making and has now been published on the Internet in the *Stanford Encyclopedia of Philosophy* (http://plato.stanford.edu/entries/chemistry/). The authors are Michael Weisberg, Robin Hendry and Paul Needham, three leading philosophers of chemistry. First of all let me say that the authors are to be applauded for taking on such an ambitious task as to summarize the whole of this relatively new field. No doubt the article will be read by many philosophers, given the prestige of this encyclopedia in the profession. In the following comments I would like to take issue with a few points in the article, and to offer some suggestions for any future revisions.

The authors begin by claiming that chemistry was founded by Aristotle, something that might well be disputed by scholars specializing in the ancient history of the sciences. The origins of chemistry, in particular, are so distant as to be practically indescribable, although many sources cite ancient Egypt as the place where chemistry was founded rather than ancient Greece. Be that as it may, the choice made by the authors is surely a reflection of the interests of Paul Needham who has written widely and eloquently on the subject of Aristotle. Needham has debated some of his views with other scholars in this journal, as in the case of the discussion with Joseph Earley.[2]

Given my own limitations on this topic I must move on to later sections of the encyclopedia article. In a large section on "substances, elements and chemical combination", we learn rather surprisingly that Lavoisier did not regard hydrogen and oxygen as elements, "although we now know they are elements". This statement is somewhat at odds with the fact that Lavoisier included both hydrogen and oxygen in his famous list of simple substances of 1789 in the Traité.

In the section that follows on Mendeleev the authors write, in passing, that many attempts were made at systematization of the elements but that an early and influential account was given by John Newlands. While it may have been an early account it is difficult to see how it might have been influential given that Newlands was ridiculed by his fellow countrymen at the London Chemical Society and remained unknown in other countries. The fact that he was belatedly awarded the Davy Medal for his work of the classification of the elements, as late as 1887, hardly amount to having produced an "influential account".

Weisberg, Hendry and Needham then choose to spell Mendeleev's first name as "Dimitrij" for reasons best known to themselves. What are normally referred to as gaps or

[2] Needham (2007) and Earley (2007).

empty spaces in Mendeleev's periodic system are unceremoniously referred to as "holes". All emphasis is placed on the predictive success of Mendeleev's work and none on his predictive failures. Moreover, no mention whatsoever is made of the long-standing debate concerning the relative value of prediction and accommodation of data in the acceptance of scientific theories and other developments generally. I am referring to a debate that has involved many historians and philosophers of science throughout the centuries and more recently such authors as Stephen Brush, John Worrall, Eric Barnes, the late Peter Lipton and Patrick Maher, all of whom discuss the periodic table in this context.

The authors of the encyclopedia article then appear to place words into the mouth of Mendeleev when they claim that he distinguished between the "end of analysis and actual components conception of elements". While the first may be true I am not aware of Mendeleev ever having having considered the more fundamental sense of 'element' in the way that the authors choose to characterize it. In fact there is an active cottage-industry within the philosophy of chemistry that has debated whether the elements are indeed components present in compounds.[3]

It is claimed that Mendeleev was able to use atomic weights as the primary ordering property of the periodic table because he assumed that the weights of compounds is the sum of the weights of the constituent atoms, as though the ordering of the elements was primarily driven by the properties of compounds rather than elements. But, even if the properties of compounds did play a role, which they did only in secondary classification into groups, it was through the concept of valence and not the additivity of atomic weights of component atoms.

The authors go on by mentioning the switch from atomic weight to atomic number as the ordering criterion that took place officially in 1923. They claim that chemists chose to do this because of "the growing recognition that electronic structure was the atomic feature responsible for governing how atoms combine to form molecules". But again, the emphasis of compound formation is in fact somewhat secondary. In choosing to focus on atomic number, which of course *may or may not* correspond to the number of electrons, chemists and physicists were following a line of research that began with van den Broek's hypothesis concerning the positive charge of on nucleus of any atom, and continued with the confirmation of that hypothesis by the work of Moseley. Compound formation, and whether or not this behavior depends on electronic structure, had little influence upon their decision to use atomic number as the ordering criterion for the elements.

In a section concerning "complications for the periodic system" the authors succeed in attributing the "…conception of the atom as comprising a positively charged nucleus around which much lighter electrons circulated…" to Bohr rather than to Rutherford or earlier precursors such as Perrin and Nagaoka. In fact Bohr merely applied the notion of quantization of angular momentum to his mentor's, Rutherford's, model of the nuclear atom.

The section ends with what I think is one of the most puzzling claims in the entire article when we learn that Paul Needham believes that the current IUPAC definition of an element in which "all isotopes showing an atomic number count as the same element" is in fact incorrect. Needham believes this because he claims that there are "salient chemical differences between isotopes". In fact the differences are, if anything, physical and even biological but not chemical. This is precisely why chemists have retained the definition that isotopes of a single element are just that, namely versions of the same element. The properties of the isotopes of hydrogen that Needham describes are very well known to

[3] For example see Earley (2009).

chemists. Nevertheless, from Paneth to the current generation of chemists, nobody would seriously contemplate Needham's proposal that "isotopes should be considered different elements"!

Section 4 of the encyclopedia article is entitled "Structure in Chemistry". In subsection 3 of this part, the authors turn to a topic which has been the basis of several sessions on philosophy of chemistry at successive meetings of the Philosophy of Science Association. The topic is essentially a replay of a debate that was carried out between the proponents of the molecular orbital and valence bond theories. As is well known the proponents of M.O. theory hold that bonding occurs but not because of directed bonds. Instead of the classical notion of electrons being shared between particular atoms, the M.O. description regarded them as being delocalized and as belonging to the entire molecule. Meanwhile the V.B. approach, in its qualitative elementary form, retains some aspects of the classical view whereby electrons hold together particular pairs or sometimes even sets of three atoms (banana bonds).

Mathematically the two approaches are equivalent. The authors of the encyclopedia article dispense with all technicalities, fail to display a single equation in their article and yet regard themselves as somehow contributing to this debate through a philosophical analysis.

In subsection 4.4 we learn about molecular structure and molecular shape. Here Robin Hendry takes over, to espouse a topic that has occupied him for about 20 years. Following authors like Woolley and so some extent Sutcliffe, Hendry claims that chemical structure, the staple of chemistry since the 19th century, cannot be reconciled with quantum mechanics.

Let me back-track a little. The Born–Oppenheimer approximation considers nuclei in a molecule to be stationary while the electrons are permitted to move. The energy of the system can then be minimized and this process can be repeated at will in order to arrive at the minimum energy. Chemists thereby find the 'structure' of the molecule which is governed by the relative positions of the nuclei. According to Woolley, and more recently Hendry, this is not good enough. In the absence of applying the Born–Oppenheimer approximation, or without fixing the positions of the nuclei, they claim that quantum mechanics fails to distinguish between the two isomers of $C_2H_6O_1$ for example. This leads Woolley and Hendry to conclude that molecular structure is somehow an alien concept, without a true quantum mechanical foundation. Woolley has claimed for many years that molecular structure does not reduce to quantum mechanics. Hendry has picked up this view and continues to champion it via an elaborate argument drawing on the work of the early 20th century British philosopher C.D. Broad. Although Hendry does not enter into much detail in the encyclopedia article, he claims categorically that molecular structure does not belong in quantum mechanics and must be "put in by hand". What he is referring to is part of a bigger problem that has long plagued the foundations of quantum mechanics, namely the problem of the collapse of the wavefunction. Hendry seems to neglect the fact that this problem has gradually begun to dissolve with the growing realization of the role of quantum decoherence in physics and other disciplines (Zurek 1991).

According to quantum mechanics, molecules can be said to be in a superposition of a number of possible structures. For example, $C_2H_6O_1$ can be regarded as a superposition of C_2H_5OH and CH_3OCH_3. Woolley, and now Hendry, concentrate on the fact that until an observation is carried out, neither of these structures has been actualized. The inference they draw from this state of affairs is that there is no intrinsic structure in the molecule, which if it were true would indeed mean that structure is not fundamental. However, the study of decoherence has shown that it is not just observations that serve to collapse the

superpositions in the quantum mechanics. The collapse can also be brought about by molecules interacting with their environment, something that Hendy occasionally mentions but quickly dismisses.

Moreover, it was traditionally believed that any collapse in the wavefunction was an instantaneous process. More recent studies have shown that decoherence takes place in a finite time, depending upon many factors. In the case of the $C_2H_6O_1$ molecule the decoherence is so rapid (about one femtosecond) as to mean that for all intents and purposes the molecule collapses into either ethanol or dimethyl ether so quickly that it wold be foolish to dwell on the brief instant when the structure is yet to settle on one of the isomers.[4] To his credit Hendry does at least hint at this possibility, although never mentioning decoherence, when he refers to Jeffrey Ramsey who has discussed the influence of the environment of molecules.

Hendry also cites Hans Primas, who lays the blame for the apparent ungroundedness of molecular structure on the fact that we usually regard molecules as being isolated systems. According to Primas, if we allow for interactions with the outside world the lack of structure evaporates. But Hendry is not impressed with either of these solutions. He continues to regard structure as a deep problem that deserves the attention of philosophers of chemistry. The only comment made in the encyclopedia article is that "there is nothing like consensus". In fact matters are quite the other way round. Nowadays it is only Hendry who seems to make a philosophical meal out of Woolley's writings. Furthermore, Hendry regards molecular structure as an emergent phenomenon and in addition believes that the structure problem reveals the workings of 'downward causation'.[5]

Weisberg, Hendry and Needham then turn to the question of reduction. This they examine in a manner that has become standard in the philosophy of chemistry, namely in terms of epistemological reduction (some prefer to call it theoretical reduction) and ontological reduction. The authors believe that any failure in epistemological reduction is not worthy of much attention. This is because a reductionist can always claim, as does Schwarz for example, that reduction could be achieved if greater computational power were made available.

The more interesting problem according to our trio of authors is whether there is any 'in principle' reason as to why chemistry cannot be reduced to quantum mechanics, even if all the computational power in the world were at the disposal of the theoretical chemist. Sure enough this may be a potentially more interesting question but one that, as I see it, cannot be answered. I say this because Hendry regularly claims that one must separate epistemological issues from ontological ones but never explains how he proposes to do this. For example, in a recent article he writes,

> … we [need to] separate the inter-theoretic and the metaphysical aspects of the reduction debate: the former concern the explanatory relationships between theories and the latter the relationships between their subject matter.
>
> This separation is necessary because there are reasons why the inter-theoretic reduction … may fail that are quite independent of any metaphysical relationship between physics and the special sciences (Hendry 2010).

[4] Here I am assuming decoherence to be synonymous with collapse of the wavefunction. This is an oversimplification but does not I believe affect the point about molecular structure that I make. I am not implying that quantum decoherence completely solves the collapse problem.

[5] Hendry (2010). In some articles Hendry has even claimed that the onus lies with the reductionist to show that downward causation does *not* occur than with authors like himself to show that something so bizarre as downward causation *does* actually exist.

Then again in the same article Hendry says,

> One obvious requirement of a criterion of ontological reduction is that whether or not it obtains must be a substantive metaphysical issue that transcends the question of what explanatory relationships exist between theories now, or might exist in the future, even though inter-theoretic relationships must continue to be relevant evidence (Hendry 2010).

But is this not something of a contradiction? How can one continue to use inter-theoretical relationships while at the same time demanding that they be separated out of ontological considerations? Actually it is not clear to me why the question of epistemological or theoretical reduction is not so important. First of all it is more accessible than the ontological question, given that there is no need to factor out theoretical considerations to just to the correct, and unspecified, degree as in the case of examining the ontological issue. Secondly, if exploring the theoretical relationship between chemical concepts and quantum mechanics reveals a gap, this can serve as a call to quantum theorists to try to affect a deeper reduction. It can also serve to trace a closer connection between chemical and quantum concepts, which might otherwise not be addressed. I believe this is the kind of thing that Hoffman has in mind and which the authors seem to approve of so highly in a different context.

Finally, in the encyclopedia article, Hendry's position is revealed when the authors write,

> Moreover, and more controversially, some philosophers of chemistry have argued that chemical properties may constrain the behavior of physical systems, something akin to what philosophers of mind call downwards causation (Kim 1999). Hendry argues that in some cases, the fact that a particular molecule has a particular molecular structure cannot be accounted for by physics. The issue arises when we consider the quantum mechanical description of structural isomers, molecules with the same atoms, but with different molecular structures. For example, methyl ether and ethanol share a Hamiltonian, the quantum mechanical description of their energetic properties. Nevertheless, they are very different molecules. Ethanol is extremely soluble in water, whereas dimethyl ether is only partially soluble in water. Ethanol boils at 78.4°C, while dimethyl ether boils at 34.6°C. Drinking ethanol leads to intoxication, while drinking dimethyl ether has no such effect. Given that quantum mechanics cannot tell us why a given collection of atoms will adopt one molecular structure (and set of chemical properties) or the other, Hendry argues that chemical properties cannot be recovered from quantum mechanical properties.

True enough quantum mechanics as a pure formalism cannot tell us. But as I mentioned earlier, quantum mechanics plus decoherence or any reasonable inclusion of the environment, or accepting that molecules are open systems, *can* explain it.

The final section is on models, an area in which Michael Weisberg has specialized. Weisberg has published a number of interesting articles on this topic while spanning various sciences including chemistry, biology and further afield.[6] However, instead of actually mentioning any specific quantum mechanical models in current use, in the

[6] However, I disagree with Weisberg's recent claim that Mendeleev's approach to the periodic system should be regarded as an example of theorizing as I argue in a forthcoming paper. While agreeing with Weisberg that Mendeleev was not acting as a modeler I know of no author who has ever suggested considering the periodic system as a theory (Weisberg 2007).

encyclopedia article, Weisberg goes to great lengths to make the obvious point that sometimes chemists prefer to use an idealized, and less accurate, model because it provides more physical insight. Although the work of Bader on bonding is mentioned in passing, nothing is said about the current debates concerning Bader and his opponents and nothing is said about actual models of chemical bonding that are very much under discussion in recent years.[7]

But as I said at the start of this comment, it takes boldness to attempt to summarize and entire field in one article. The authors have broken new ground which will serve as a departure point for further discussion.

Finally, just a reminder that out annual ISPC meeting is being held in Latin America for the first time. This will take place at the Universidad de Los Andes in Bogota, Colombia. Please see following announcement from the organizer, Guillermo Restrepo.

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[7] Frenking and Shaik (2007).