

## La Química en el siglo XX y lo que nos depara el siglo XXI

# On The Nature of Chemistry

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The very nature of chemistry presents us with a tension. A tension between the exhilaration of diversity of substances and forms on the one hand and the safety of fundamental unity on the other. Even just the recent history of chemistry has been all about this tension, from the debates about Prout's hypothesis as to whether there is a primary matter in the 19th century to the more recent speculations as to whether computers will enable us to virtually dispense with experimental chemistry.

The tension between plurality and unity is one which people who become chemists seem to be able to live with. Those who cannot tend to gravitate towards physics or anything else for that matter. But to onlookers trying to understand the nature of science chemistry presents an essentially philosophical paradox of how the "many and the one" can co-exist. The French philosopher-chemist Gaston Bachelard has expressed this condition in the title of one of his earlier books, *Le Pluralisme Coherent de la Chimie Moderne*.

To chemical educators this tension which I have alluded to lies at the heart of many debates as to how chemistry should be presented. Should we begin with the sheer diversity of substances and reactions, by emphasizing qualitative chemistry or should we put unifying theories to the fore and only later hang the chemical facts on these general principles?

These are issues which were all being actively debated in the 19th century when chemistry and physics were undergoing rapid changes. Today one hears little overt discussion of these issues although

like all deep philosophical questions the question of the many and the one lies at the heart of many specific issues which are discussed as if they were of an entirely practical nature.

Whereas the terms philosophy of chemistry and chemical philosophy were frequently used in the titles of books and treatises from the seventeenth to the nineteenth century one finds very little reference to the terms nowadays (Nye, 1995). Even philosophy of science, the academic study of the nature of science, appears to have neglected this and other philosophical aspects of chemistry. Until relatively recently there was no subdiscipline devoted specifically to the kinds of problems raised by the chemical sciences (Scerri, 1997, Scerri, McIntyre, 1997).

But no science can be completely divorced from its philosophical and historical roots and even if practicing chemists may sometimes think that these aspects have no role to play, this is clearly shortsighted. In any case there can be no excuse for philosophers of science to simply ignore the philosophical nature of chemistry when trying to understand the nature of science in general.

The question of "the one and the many" goes by many names. One approach, especially prominent in philosophy, has been to use the term reduction. But even here a simple word conveys many different meanings to different people. In its broadest terms reduction can mean the recognition of an element of similarity between two or more phenomena which leads us to realize some common features which the phenomena share. Diversity appears to have been quite literally 'reduced'. Seen from a different perspective reduction is taken to mean the very act of breaking up a system into smaller pieces in order to examine its parts and thereby gain a deeper understanding of it. Here the notion of reduction seems to be almost synonymous with analysis and this has been the over-riding characteristic of modern science, as opposed to the purely contemplative approach of the ancient Greek philosophers for example. Anyone working in science is practicing reduction, that is practicing an analysis of parts in the hope of understanding the entire system. Whether this approach is entirely successful is another ques-

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A comprehensive bibliography on Philosophy of Chemistry compiled by E.R. Scerri can be found in the special issue of *Synthese*, 111, 3, 1997.

tion and ones liking or otherwise for the reductive approach must ultimately remain in the realm of subjective choice. However, there is no denying that even attempts to reduce by analysis of parts, whether fully successful or not, are invariably productive in the sense of providing useful spin-offs. The scientific approach which I am calling reduction consists of an analysis of the smallest parts is an unending quest despite the periodic pronouncements that we may have reached the end of physics or even the end of science (Horgan, 1996). Elementary particle physics, were it not for the exorbitant costs involved, would continue to examine matter and energy at progressively finer levels and the knowledge gained would eventually trickle down to the 'less fundamental' sciences such as solid state physics, quantum chemistry, molecular biology and so on. One recent example has been the suggestion that parity violation in the weak nuclear force may be responsible for the asymmetry in the amounts of d and l forms of most chiral compounds observed in nature

Another topical example is to be found in contemporary molecular biology where the current obsession is the search for the human genome. Here the thinking seems to be that once the genome has been fully determined we will have arrived at rock-bottom and biology will have been essentially completed. Of course this kind of thinking is partly propaganda for extracting funds from government agencies. Once the human genome is fully mapped, or while still in the course of this process, it will emerge that a whole new realm of structure and information lies at a deeper level, just waiting to be discovered and offering the promise of yet better medical, biological and perhaps even social benefits.

### Metaphysics and metachemistry

One of the areas traditionally studied in philosophy is Metaphysics which aims to discover what exists, for example whether God or any other supreme being exists, what entities exist in the world and so on. These are questions which do not necessarily rely on empirical investigations and so tend to be frowned upon by scientists who pride themselves on having solid foundations in observational data.

But this attitude shown by many modern scientists might itself derive from a philosophical prejudice on their part and one which is now rather outdated. It seems to derive, in part, from the Logical Positivist school of philosophy which flourished in the early and middle part of the twentieth century

and attempted to completely banish all metaphysics as being meaningless. However, the logical positivist program of providing an observational base for all of science has failed for various technical reasons which will not be pursued in the present article. Philosophers, and philosophers of science in particular, have shown a greater tendency to pursue metaphysical questions following the criticisms of logical positivism and logical empiricism made initially by the likes of Quine, Popper, Kuhn, Feyerabend and Lakatos among others.

Indeed there are several areas in recent chemical thought which I would like to argue have been primarily concerned with metaphysical issues although this has not always been explicitly acknowledged.

### Resonance

For example, in the 1950's the notion of quantum mechanical resonance as developed by Linus Pauling on the basis of earlier work by Heisenberg produced a serious scientific controversy in the then Soviet Union. This issue hinged on whether the resonance structures postulated by Pauling's valence bond theory actually existed or not. Admittedly this was a debate was largely motivated by political factors concerning the official Soviet policy of supporting dialectical materialism. This philosophical position seemed to leave no room for resonating chemical structures which according to some interpretations did not actually 'exist'. Some philosophical analyses of this issue have been provided by van Meeren and Hargittai (Vanmeeren, 1986, Hargittai, 1995).

### Orbitals

A few years ago a controversy erupted in a chemical education journal, following the publication of an article by Ogilvie in which he claimed in his subtitle that "there are no such things as orbitals" (Ogilvie, 1990). This article was, in part, an attack on the views of Pauling which Ogilvie claimed were continuing to cause problems in the manner in which chemistry is taught. The article provoked a number of responses including one from Pauling himself in which he unrelentingly defended his original views (Pauling, 1992, Scerri, 1992, Scott, 1992).

Ogilvie's main claim for the non-existence of orbitals appears to hinge on the fact that there are several formulations of quantum mechanics including, at the most elementary level, Heisenberg's matrix mechanics and Schrödinger's wave mecha-

nics. Ogilvie maintains that orbitals cannot be regarded as being fundamental since they only emerge from one of these formulations, namely Schrödinger's wave mechanics. However, throughout his long and detailed article he fails to cite the one important criterion which renders the existence of orbitals redundant even *within* the Schrödinger formulation. This occurs because the assignment of quantum numbers is strictly invalid in many-electron atoms. Instead of concentrating on the startling announcement in his subtitle, "There are no such things as orbitals", Ogilvie proceeds to argue for the lack of experimental evidence for the real existence of hybrid orbitals in molecules such as methane.

Pauling's response to Ogilvie in a later issue of the same journal consists mainly of an *ad hominem* assault in which he accuses Ogilvie of failing to understand quantum mechanics. One rather interesting remark made by Pauling in response to Ogilvie's claim that orbitals do not exist is the following,

The subheading of the Ogilvie paper "There Are No Such Things As Orbitals!" contains a misconception of the meaning of the word "thing". One of the dictionary definitions of thing is "Anything that is or may become an object of thought;" in other words, a thing need not be tangible, but it could be represented by a symbol... Quantum mechanical expressions for orbitals, such as those that Mulliken and I and scores of other theoretical physicists have formulated, are clearly objects of thought, and hence are things (Pauling, 1992, 520).

One does not need to be a philosopher to appreciate the folly of Pauling's remark. Surely the mere fact that unicorns and fairies, for the sake of argument, might be objects of thought does not imply that they exist in the real world. One wonders whether Pauling would have accepted a subheading which had simply stated "Orbitals do not exist" which would have avoided the use of the word "thing" and would still have conveyed Ogilvie's intention.

Although this particular controversy was terminated by editorial fiat, the question of how to teach chemistry and in particular whether to put quantum mechanics, before the chemical facts, continues to be a source of discussion in chemical education circles (Basolo, Parry, 1980; Bent, 1984, 1987; Gallup, 1988; Gillespie *et al.*, 1996; Hudson, 1980; Pilar, 1981; Sanderson, 1986; Scaffrath, 1983; Zuckerman, 1986). In previous articles I sought to remind chemical educators that the orbital concept which is so prevalent in chemistry is not underwritten by theoretical physics,

and in particular quantum mechanics, from which the concept is commonly supposed to emerge. I implied that chemical educators were mistaken in emphasizing atomic structure and quantum mechanics thus putting physics before chemistry, since the orbital concept which chemists concentrate their attention upon, does not in fact 'exist' (Scerri, 1991).

I was emphasizing as some philosophers of science might, that the term orbital does not refer according to quantum mechanics. That is to say, according to quantum mechanics à la Schrödinger and Heisenberg, orbitals should not be regarded realistically although in the old quantum theory orbits, as they were then termed, could be so interpreted. I therefore urged a partial return to teaching chemistry according to qualitative concepts rather than falling prey to the seductive influence of quantum mechanics and atomic structure. Recently I have come to a new view of these matters, which I now turn to.

First of all, it would appear that the use of orbitals and configurations in chemistry has continued to increase and the chances for a return to the nostalgic days of chemistry based upon 'smells, bangs and colors' appear increasingly dimmer. However, there is a deeper philosophical reason why one should stay loyal to orbitals in chemistry education while at the same time not committing any errors from the point of view of quantum mechanics. I believe that in pronouncing on the situation from the perspective of theoretical physics I was myself falling prey to the ever lingering reductionist view which considers that physics rules all of science, or what has sometimes been termed 'physics imperialism'. A more enlightened way to regard such questions would be to "bite the bullet" and assert that physics imperialism is at fault and that the special sciences are, as I suggested above, autonomous and thus not entirely dependent upon the latest pronouncements from theoretical physics (Scerri, 2000).

### Structure

Last but not least, there has been an ongoing controversy regarding whether or not molecular structure has any objective existence or whether it is merely a metaphor. Woolley and other authors have suggested that the concept of molecular structure, which is so central to modern chemistry, is nothing but a metaphor which has no objective reality at the quantum mechanical level. The basis of this claim lies in the fact that the appropriate Hamiltonian for a molecule



Paolo Gandolfi, *Peregrinazione Magica*, 1995. Tomada de *The Sciences*, marzo-abril, 1998.

such as  $C_3H_4$  only contains terms describing interactions between protons and electrons in the system. The structure of the molecule or relative positions of the nuclei is introduced somewhat artificially in calculations, it is claimed, by invoking the Born-Oppenheimer approximation. Woolley and some others have claimed that a purely quantum mechanical which involves the raw molecular Hamiltonian does not therefore require the attribution of any structure to molecules. In addition, the three known isomers of  $C_3H_4$  all share the same Hamiltonian with the implication that a purely quantum mechanical calculation without the Born-Oppenheimer approximation cannot distinguish between the three distinct structures which are believed to exist. Nor it is claimed are such considerations purely academic, since as Woolley has pointed out there are many cases in which calculations carried out without the Born-Oppenheimer approximation yield predictions which are more accurate than those carried out in the more conventional approach which does make use of the approximation.

Most chemists have reacted to the view that structure is nothing but a metaphor with complete incredulity while pointing out the seemingly overwhelming evidence for structure which comes from spectroscopic and other structural studies. They fur-

her suggest that if a deep quantum mechanical analysis reveals molecular structure to be a mathematical artifact then the fault must lie with present-day quantum mechanics and not with the chemical notion of structure. Interestingly, a philosopher of science has recently sided with the traditional chemical view in upholding the reality of molecular structure. Ramsey has argued that a careful analysis of the work of Woolley and some other chemical heretics reveals that they are themselves misinterpreting what it means to hold realistic views about scientific entities (Ramsey, 1997).

It should also be mentioned that Bader and co-workers have developed a research program in which they attempt to connect classical chemical concepts such as molecular structure to the principles of quantum mechanics (Bader, 1990). The claim is that this goal has been achieved without any intrusions from the kinds of problems raised by Woolley and others like him. It remains to be seen whether a careful analysis by philosophers of chemistry might shed some new light on this emerging debate.

### Conclusion

So even just in staying within the area of metaphysics we see many relevant questions which suggest them-

selves for study by philosophy of chemistry. If we were to turn our attention to the epistemological aspects of philosophy we would find another series of interesting topics such as the question of whether chemical theories reduce to quantum mechanics and the nature of chemical explanations within the wider context of theories of explanation developed by philosophers of science (Scerri, McIntyre, 1997, Scerri, 1997a, 1997b, 1997c, 1997d, Scerri, 1998a, 1998b). But these epistemological issues must await a future article since there is much material to consider and it cannot be dealt with briefly. ▣

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