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Scientific Realism and the History of Chemistry

Robin Findlay Hendry*

I. EPHEMERAL SCIENCE?

Do scientific theories build cumulatively on the achievements of their predecessors, or do they sweep them away in favour of new theoretical visions? Philosophers are sometimes accused—by scientists, and by philosophers—of generating pseudoquestions by imposing their own abstractions on science. The question of theoretical cumulativeness is not like that, for it has been raised by people who are not (or not primarily) philosophers. Here for instance is Henri Poincaré on the “bankruptcy of science”:

The ephemeral nature of scientific theories takes by surprise the man of the world. Their brief period of prosperity ended, he sees them abandoned one after another; he sees ruins piled upon ruins; he predicts that the theories in fashion to-day will in a short time succumb in their turn, and he concludes that they are absolutely in vain. This is what he calls the bankruptcy of science. (Poincaré 1905, 178)

It is well known among philosophers that Poincaré, having identified that pessimistic line of thought, went on to reject it, at least partially. It is not so well known among philosophers that some thirty years later,¹ in his Presidential Address to the Chemical Society (later to become the Royal Society of Chemistry), Nevil Sidgwick sketched a much more robust defence of cumulativeness in the development of theories of chemical structure:

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¹ I do not know whether Poincaré’s musings had any influence on Sidgwick’s, whether direct or indirect.

There are two ideas about the progress of science which are widely prevalent, and which appear to me to be both false and pernicious. The first is the notion that when a new discovery is made, it shows the previous conceptions on the subject to be untrue; from which unscientific people draw the very natural conclusion that if to-day's scientific ideas show those of yesterday to be wrong, we need not trouble about them, because they may themselves be shown to be wrong to-morrow. It is difficult to imagine any statement more opposed to the facts. The progress of knowledge does indeed correct certain details in our ideas, but the main result of every great discovery is to establish the existing doctrines on a firmer foundation, and give them a deeper meaning. (Sidgwick 1936, 533)

Leaving aside the second of his pernicious falsehoods, Sidgwick's conclusion is forthright:

I hope I have said enough to show that the modern development of the structural theory, far from destroying the older doctrine, has given it a longer and a fuller life; and further that the tendency of modern research is not to contract the scope of its material, but on the contrary to call in to its assistance an increasingly wide range of properties, and to bring to bear on its problems the results of every kind of physical and chemical investigation. (Sidgwick 1936, 538)

Sidgwick's thoughts suggest a bold historiographical hypothesis, whose relevance to the current debate on scientific realism should be obvious: that theories of structure and composition have, since the 1860s, developed through a series of conservative extensions, despite some apparently radical theoretical and conceptual change during this time. A conservative extension of a theory is one where its inferential content *before* the extension (i.e., that which determines its explanatory and predictive power) is a proper subset of its inferential content afterwards.² This will happen, for instance, when a theory is extended or reinterpreted so as to allow inferences to be made about a new range of phenomena.

² Mauricio Suárez (2004) presents a deflationary account of representation: inferential use exhausts what can usefully be said about representation. Whether or not one agrees with that, inference is certainly a very useful way to track the interpretation of a representation by its users.

II. STABILITY AND STRUCTURE

Of course our bold historiographical claim is really a *sequence* of hypotheses concerning the retention of specific structural features attributed by chemists to molecules. Four key developments suggest themselves for further study: the emergence of structural formulae to account for isomerism in the 1860s; the extension of structure into three dimensions in the 1870s; integration with physical theories and experimental methods in the early twentieth century; and the advent of quantum mechanics from the 1930s onwards.

Bond structure in organic chemistry (1860s)

As a body of theory, molecular structure presents a number of apparent difficulties for historians and philosophers of science, posed by its presentation, and by its interpretation. These difficulties can be addressed if we pay careful attention to the inferential *uses* to which the various visual representations are put, and which reflect sophisticated interpretative stances that the chemists took toward their representational schemes.

Presentation: In organic chemistry, structures were represented using a diverse range of representational media, including August Kekulé's sausage formulae, A.W. Hofmann's "glyptic formulae" and the chemical graphs of Alexander Crum Brown and Edward Frankland (for examples see Rocke 2010, ch. 5). Moreover the *visual* nature of these representations (as opposed to, say, mathematical equations) can make it difficult to identify the predictive and explanatory content of the theory. Nevertheless, underlying this diversity of presentation was a relatively unified body of theory, based on the core idea of fixed atomic valences generating a fixed number of ways a given collection of atoms of different kinds can be connected together via bonds (see Rocke 1984, 2010).

Interpretation: The theory was developed amid considerable controversy concerning the reality of atoms (see Brock and Knight 1967), and whether hypotheses about structure at the atomic scale could have any legitimate role in chemistry. The resulting interpretative caution among the chemists of the time has been understood by historians and philosophers as a form of instrumentalism. It was that, but the label could obscure finer interpretative distinctions to be observed in the way the theories were being used. Like many chemists at the time, Frankland was careful to point out that structural formulae were intended "to represent neither the shape of the molecules, nor the relative position of the constituent atoms" (see Biggs et al. 1976, 59). William Brock and David Knight have described Frankland as one of the "moderate conventionalists" about structural formulae, people who are "prepared to employ them as useful fictions" (1967, 21). Elsewhere (2010) I

have argued that Frankland's stance also reflects an awareness that the use of structural formulae in chemical explanations required inferences to be made only concerning the order of the connections between the atoms as they affect the identity or diversity of different substances. Although the representations carry excess content, Frankland would make inferences only concerning the bond topology:

The lines connecting the different atoms of a compound, and which might with equal propriety be drawn in any other direction, provided they connected together the same elements, serve only to show the definite disposal of the bonds: thus the formula for nitric acid indicates that two of the three constituent atoms of oxygen are combined with nitrogen alone, whilst the third oxygen atom is combined both with nitrogen and hydrogen. (Frankland, quoted in Biggs et al. 1976, 59)

The shapes of the molecules and the relative positions of the atoms played no more part in the representation than the particular colours chosen to represent the different kinds of atoms in Hofmann's glyptic formulae. All of this reflects the conventionalist's awareness that a given "fiction" will be useful for some things and not for others.

Stereochemistry (1870s)

The explanatory scope of the structural formulae was soon extended so that inferences *could* be made about the relative positions of the atoms in a molecule. In 1874, Jacobus van 't Hoff explained why there are two isomers of compounds in which four different groups are attached to a single carbon atom by supposing that the valences are arranged tetrahedrally (with the two isomers conceived of as mirror images of each other). Adolf von Baeyer explained the instability and reactivity of some organic compounds by reference to strain in their molecules, which meant their distortion away from some preferred structure (see Ramberg 2003, Chs. 3 and 4). These stereochemical theories were intrinsically spatial, because their explanatory power depended precisely on their describing the arrangement of atoms in space. The extension of the theory did not require a wholesale revision of the structures that had previously been assigned to organic substances: they were simply embedded in space, allowing new classes of inference to be made. Hence stereochemistry constituted a conservative extension of the earlier structural theory of the 1860s.

Structure in motion (1920s onwards)

The structural formulae of the nineteenth century are sometimes described as static. This can be misleading. Nineteenth-century chemists

clearly entertained the thought that matter must be dynamic at the atomic scale, but they had no means to make reliable inferences about any such motions. Hence they did not make any. The structural *formulae* may have been static, but they were not interpreted as representing *molecules* to be static. This caution began to change in the twentieth century. In 1911, Nils Bjerrum applied the “old” quantum theory to the motions of molecules and their interaction with radiation, potentially explaining their spectroscopic behaviour (see Assmus 1992). From the 1920s onwards, Christopher Ingold and others applied G.N. Lewis’s understanding of the covalent bond as deriving from the sharing of electrons to give detailed insight into reaction mechanisms. These explained *how*, when chemical reactions occur, the structure of the reagents transforms into the structure of the products (see Brock 1992, ch. 14; Goodwin 2007). These developments were based on conservative extensions of the structures that emerged in the nineteenth century, allowing inferences to be made about their motions, and providing explanations of various spectroscopic and kinetic phenomena that had not previously been within the scope of structural theory.

Quantum chemistry

What prospects are there for extending this argument into the era of quantum mechanics? This might seem like a hopeless task: surely the quantum-mechanical molecule is radically different from the classical one! But this is too quick. Firstly, “classical” chemical structures are not classical in any way that has a direct connection with physics. They involve no application of (for instance) classical mechanics or Boltzmann statistics. Secondly, when quantum mechanics did come to be applied to molecules in the 1920s and 30s, the resultant Schrödinger equations were insoluble. To make progress, chemists and physicists developed semi-empirical methods that amounted to retaining classical structure by simple inclusion. This is why Linus Pauling, for instance, regarded quantum chemistry as a synthesis of “classical” structure and quantum mechanics (for details see Hendry 2010). By the 1980s, the development of density-functional theory allowed theoretical chemists to compute accurate electron-density distributions for molecules, which were used by Richard Bader (1990) to define structures which could be interpreted as corresponding to the traditional atoms and bond topologies of molecules. The details are quite interesting: for a given molecule, use its electron-density distribution to define “bond paths” between atoms. These bond paths generate a “molecular graph” for the molecule. In many cases the resulting molecular graph is strikingly close to the

classical structure for the molecule.³ As Bader puts it, “The recovery of a chemical structure in terms of a property of the system’s charge density is a most remarkable and important result” (1990, 33). But the correspondence between bond path and chemical bond is not perfect. The main problems concern *repulsive* (rather than attractive) interactions between neighbouring atoms in a molecule. Bader’s algorithm finds bond paths corresponding to these repulsive interactions, even though chemists would not normally regard the mutually repelling pairs of atoms as bonded to each other. One response is to defend these “bonds” as bonds (see Bader 2006), which looks like bullet-biting. Too much of that will undermine the revisionary analysis one is seeking to defend.

III. STRUCTURE AND SCIENTIFIC REALISM

I will conclude with brief discussions of three ways in which I think the historical development of structural theory can inform scientific realism.

Pessimistic induction

The development of structural theory from the 1860s to the 1920s would seem to provide a refreshing contrast to the historical case studies usually cited as grounds for pessimistic induction. Frankland was able to identify which features of his representations should be taken seriously, and more than 150 years later these very features are preserved. Perhaps structure in chemistry supports, rather than confutes, the cumulativeness of science. The arrival of quantum chemistry provides a more complex example. In the early years, the best explanation of the retention of classical structure in the quantum-mechanical molecular models is no doubt chemists’ wish to find it there, and their resulting inclusion of it “by hand.” No realist inference seems required. On the other hand, Bader’s results seem to show something significant, but just what they show depends on the details of his algorithm. How loose or strict are the constraints on defining molecular graphs? How many independent parameters are there? How significant, from an ontological point of view, is electron density, the quantity in terms of which the molecular graphs are defined? How troubling are the false positives, the bonds found by the algorithm where no chemist would put them? On all these desiderata except the last, I would argue that Bader’s algorithm scores highly.

³ Bader (1990, 72-3) provides molecular graphs for an impressive range of aliphatic hydrocarbons.

Unconceived alternatives

Structural theory is also relevant to Kyle Stanford's skeptical view of eliminative inference (2006), in two ways: firstly, van 't Hoff arrived at his version of structural theory via eliminative reasoning; secondly, eliminative reasoning in modern chemistry works within a framework of structural possibility defined by this theory. How did van 't Hoff arrive at the tetrahedron? Following Johannes Wislicenus, he argued first that it was possible to account for the observed number and variety of the isomers of certain organic substances only by taking into account the arrangement of atoms in space. He then defended a tetrahedral geometry for the carbon atom by rejecting a square planar arrangement: if carbon's geometry were square planar, there would be more isomers of substituted methane than are observed.⁴ Assuming a tetrahedral arrangement, in contrast, would be in accord with the observed number of isomers (see Brock 1992, 260). The structural theory developed in the 1870s still provides the space of theoretical possibility within which the normal science of structural thinking is pursued. Roald Hoffmann (1995, ch. 29) provides a beautiful example of explicitly eliminative reasoning in his discussion of how H. Okabe and J. R. McNesby used isotopic labelling to eliminate two out of three possible mechanisms for the photolysis of ethane to ethylene.

While Stanford seeks to circumscribe the skeptical problem that unconceived alternatives pose for eliminative inference (2006, 32), here we have everyday scientific inferences that could be expected to be reliable just in case we can trust a broad framework of theory that was itself arrived at by elimination. Is Hoffmann allowed his inference? What is also striking is the extent to which, between the 1860s and the 1950s, molecular structure became much less remote from experience. In the 1860s, structures were regarded as highly speculative, like string theory today. Rightly so: the sole basis for attributing a structure to a substance was the inferences this would allow one to make about the chemical reactions it would undergo. Through the successive introduction of X-ray diffraction, infrared spectroscopy, and nuclear magnetic resonance spectroscopy (and more importantly their mutual reinforcement), molecular structures became the objects of (indirect) observation. But if eliminative reasoning is so unreliable, this should be surprising. How lucky for us that those Victorian chemists were able to conceive of the theoretical possibilities that would underwrite a hundred years of conservative extension, and would be vindicated by indirect observation via physical methods whose existence was unimaginable at the time. Or perhaps van 't Hoff's reasoning was reliable. It is plausible that

⁴ For instance, disubstituted methane (of the form CH_2X_2) would have two isomers if it were square planar, whereas only one could be found.

eliminative reasoning is reliable to different extents in different contexts, but the question is, what makes the difference? Of its very nature, structural and geometrical possibility may just have been more amenable to eliminative reasoning as wielded by a nineteenth-century chemist than the spaces of theoretical possibility appearing in Stanford's own examples (early thinking about mechanisms of biological heritability). Or maybe epistemic luck plays a role: the historically contingent development of organic chemistry during the nineteenth century delivers to van 't Hoff as a plausible assumption the very premise that would render an eliminative inference valid.

The ontological reliability of the special sciences

It is common among both philosophers and scientists to entertain the possibility that classical molecular structure is but a figment, a heuristic device that worked well enough for the nineteenth century but must be discarded today, at least as describing a real feature of the world. The basis for the rejection is its supposed incompatibility with quantum mechanics, which presents us with a microscopic world of Heraclitean strangeness that cannot accommodate the balls and sticks of molecular structure. I think this is a misinterpretation of both molecular structure and of quantum mechanics (at least as that theory is applied by physicists), but it seems additionally unfair given just how *long* structural theory has been around. Here is a line of thought to counter this epistemic injustice: if structural thinking in chemistry really is as cumulative as it seems,⁵ this would also make it an interesting contrast with physics, within which philosophers have sometimes struggled to identify continuity across theory change. Chemistry interprets its theories in ways that render them solid enough to constitute a lasting foundation for later achievements, unlike its neighbouring discipline, now revealed as a flighty follower of ontological fashion. Maybe the difference is in the interpretative caution. To dispassionate observers, some parts of physics (and the philosophy of physics) seem to get lost in a thicket of speculative metaphysical hypotheses generated by taking far too seriously abstract mathematical features of the dynamics of fundamental theories (multiverses, wavefunctions in 3N-dimensional configuration space replacing 3-dimensional space, etc.), even though the truth or falsity of those speculative hypotheses could make no difference to the reasoning that makes those theories testable.⁶ Chemistry has long regarded itself as cautious and

⁵ I have not even mentioned the remarkable stability of compositional claims about compound substances since the chemical revolution. Nor have I discussed in any detail how commensuration with physics genuinely deepened structural explanation in chemistry, as Sidgwick argued.

⁶ I was once told by a philosopher of physics that I could stop worrying about the problem of reducing molecular structure to physics if only I could embrace the multiverse.

pragmatic, and chooses to be serious only about the parts of its theories with which it can make inferences. Perhaps philosophers should also be wary of regarding physics as the only “ontological science”, and should be cautious about overwriting the results of the special sciences with (possibly highly revisionary) reinterpretations based on the latest speculative interpretation of a physical theory. The problem is not with physics or physical theory, but with where we focus our ontological attention: we should not prioritize the axioms of a theory over its applications, when it is in the latter that all the empirical support is earned.

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REFERENCES

- Assmus, Alexi. 1992. The Molecular Tradition in Early Quantum Theory. *Historical Studies in the Physical and Biological Sciences* 22(2): 209-231.
- Bader, Richard F.W. 1990. *Atoms in Molecules: A Quantum Theory*. Oxford: Oxford University Press.
- Bader, Richard F.W. 2006. Pauli Repulsions Exist Only in the Eye of the Beholder. *Chemistry: A European Journal* 12(10): 2896-901.
- Biggs, Norman L., E. Keith Lloyd and Robin J. Wilson. 1976. *Graph Theory 1736-1936*. Oxford: Clarendon Press.
- Brock, William H. 1992. *The Fontana History of Chemistry*. London: Fontana Press.
- Brock, William H. and David M. Knight. 1967. The Atomic Debates. In *The Atomic Debates: Brodie and the Rejection of Atomic Theory, Three Studies*, ed. W.H. Brock, 1-30. Leicester: Leicester University Press.
- Goodwin, W.M. 2007. Scientific Understanding After the Ingold Revolution in Organic Chemistry. *Philosophy of Science* 74(3): 386-408.
- Hendry, Robin Findlay. 2010. The Chemical Bond: Structure, Energy and Explanation. In *EPSA Philosophical Issues in the Sciences: Launch of the European Philosophy of Science Association*, eds. Mauro Dorato, Miklós Rédei and Mauricio Suárez, 117-127. Berlin: Springer.
- Hoffmann, Roald. 1995. *The Same and Not the Same*. New York: Columbia University Press.
- Poincaré, Henri. 1905. *Science and Hypothesis*. London: Walter Scott.

- Ramberg, Peter. 2003. *Chemical Structure, Spatial Arrangement: The Early History of Stereochemistry, 1874-1914*. Aldershot: Ashgate.
- Rocke, Alan J. 1984. *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*. Columbus: Ohio State University Press.
- Rocke, Alan J. 2010. *Image and Reality: Kekulé, Kopp and the Scientific Imagination*. Chicago: Chicago University Press.
- Sidgwick, N.V. 1936. Structural Chemistry. *Journal of the Chemical Society* 149: 533-538.
- Stanford, P. Kyle. 2006. *Exceeding our Grasp: Science, History and the Problem of Unconceived Alternatives*. Oxford: Oxford University Press.
- Suárez, Mauricio. 2004. An Inferential Conception of Scientific Representation. *Philosophy of Science* 71(5): 767-779.