

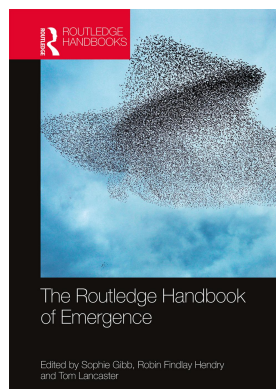
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EMERGENCE IN CHEMISTRY

Substance and structure

*Robin Findlay Hendry***Introduction**

Chemistry has a history in the emergence debate. Even before the term ‘emergence’ acquired its modern philosophical meaning, John Stuart Mill cited chemical compounds as the bearers of emergent properties that could not be predicted from those of their constituent elements. Mill’s successors in the philosophical tradition that Brian McLaughlin has called ‘British Emergentism’, including C.D. Broad, followed him (McLaughlin 1992). Chemistry is not now widely cited as a rich source of candidate examples of emergence. The debate has moved on in two ways. First, the emergence debate has moved beyond the epistemic criteria for emergence they applied, such as predictability. Second, many philosophers and scientists would no doubt agree with McLaughlin’s judgement that the advent of quantum mechanics in the 1920s, and the explanatory advances that came in its wake, rendered the British Emergentists’ central claims about chemistry ‘enormously implausible’ (McLaughlin 1992, 89).

There should be no doubt about how important the scientific advances were that unified chemistry and physics in the twentieth century. During the nineteenth century, chemists had established that chemical substances are composed of a finite number of more basic substances: the chemical elements. To account for the existence of isomers – distinct chemical substances which are composed of the same elements in the same proportions – chemists developed theories of structure. The structures were the different *ways* in which the same elements are combined within them. In the early twentieth century, investigations of atomic structure offered a physical account of the nature of the elements: they are essentially classes of atoms which are alike with respect to their nuclear charge, but which may differ with respect to their mass. G.N. Lewis then offered an account of how bonds are realised by shared electrons. Although this identification produced many novel insights into the mechanisms of chemical reactions, especially in organic chemistry, Lewis’ work was (so the story goes) in its turn superseded by the advent of quantum mechanics.

In what follows I will argue that chemistry is a far more fertile ground for emergence than many scientists and philosophers allow. Chemistry studies substances, accounting for their chemical and spectroscopic behaviour in terms of their structure. There is scope for seeing substances themselves as emergent, and bearing emergent causal powers, with respect to the populations of molecular species of which they are composed. Structures themselves are emergent from dynamical processes within molecular populations: different structures emerge at different scales of energy, time and length, and there is no reason to privilege processes at higher energies or shorter lengths – or timescales. Finally, there are no purely scientific reasons to believe that molecular structure is determined

to exist by the quantum mechanics of systems of electrons and nuclei. The emergence of quantum chemistry – the application of quantum-mechanical principles to systems of electrons and nuclei – was not a deductive affair and offers no grounds for ruling out emergence in chemistry. Structures arise and persist within special dynamical conditions. Quantum mechanics provides not a derivation of structure, but a precise identification of the conditions under which it can exist.

Emergence and reducibility

In the most abstract terms, emergence is dependent novelty: A emerges from B when it is dependent and yet also novel or autonomous with respect to B. More specific varieties of emergence result when particular kinds of dependence and novelty are filled in. Thus, for instance, A might depend on B in the sense that it could not exist without B. This kind of weak ontological dependence is compatible with A being novel or autonomous with respect to B in a number of ways. Perhaps A's existence cannot in principle be predicted on the basis of B; or perhaps B can give rise to A only in the presence of certain substantive conditions, so that the mere existence of B does not entail A's existence.

There is also a long tradition according to which emergence is contrasted with reducibility; hence, reduction is also an important notion to consider. Twentieth-century discussions of emergence concentrated on intertheoretic reducibility, conceived of as the derivability of chemical theories from more fundamental physical theories (Nagel 1979). Intertheoretic reduction clearly excludes emergence: A cannot be novel or autonomous with respect to B if it is entailed by it. Yet intertheoretic reduction is a tall order. Applying physical theories such as quantum mechanics to chemical systems such as atoms and molecules yields complicated and computationally intractable equations, so chemists and physicists introduce models and approximations that simplify the exact equations or replace them entirely. Hence, the failure of strict intertheoretic reduction might be explained in two different ways. Reductionists tend to see the failure of derivability as expressing our limited mathematical abilities; models and approximations are proxies for the exact laws, with no independent explanatory power (Hendry 1998).¹ In contrast, emergentists tend to see the failure of derivability as showing the need to identify substantive further conditions for the existence of the phenomena they are attempting to explain. When a special science such as chemistry applies general physical theories to the study of emergent phenomena, the construction of physical models explaining these phenomena will take the form of a synthesis of physical and special-science principles, rather than a derivation of one from the other.²

Since reductionists and emergentists may agree that explanatorily relevant facts about B cannot be derived from theories concerning A, yet disagree on whether this is a sign of A's ontological autonomy, how might we express their disagreement? Ideally it should involve contrasting views of reality – different metaphysical accounts of how the world is, expressed in terms that transcend any claims about logical relationships between theories. In the metaphysics of mind, strong emergence has come to be associated with the existence of novel causal powers. Our understanding of the ontological relationship between chemistry and physics can learn from this and then feed back into metaphysics and the philosophy of mind, showing how the existence of novel causal powers is much less exotic or mysterious than many philosophers take it to be (for argument see Hendry 2006a, 2010a).

Chemical substances are emergent

Many philosophers might reject the idea that there can be strong emergence in chemistry because they think that the reducibility of chemical entities and properties to physical entities and properties, or their identity with physical entities and properties, has been established and expressed in

such theoretical identities as ‘water is H_2O ’. The argument is supposed to be that ‘water is H_2O ’ should be read as ‘water = H_2O ’. To be H_2O *just is* to be composed of H_2O molecules. This settles the emergence debate, because if the contents of a particular jug have any causal powers in virtue of being water (e.g. the power to quench thirst or to dissolve salt), then those contents have those powers in virtue of their being composed of H_2O molecules. From a range of different perspectives, the claim that ‘water is H_2O ’ has been challenged by Barbara Malt (1994), Paul Needham (2000, 2002, 2011), Jaap van Brakel (2000), Michael Weisberg (2006) and Hasok Chang (2012). I would not challenge the identity, so long as it is properly construed. I have argued elsewhere that chemical substances are individuated by their microstructural properties and relations (see Hendry 2006b), that the identity of water with H_2O can be said to have been discovered³ and that a substance’s structure at the molecular scale *is what makes it the substance that it is* from a chemical point of view (see Hendry 2016a). However, I will argue that it is a straightforward misreading of ‘water is H_2O ’ to think that it establishes the reducibility of water, or some chemical analogue of the mind–brain identity theory.

Historically, the microstructural identity of water was established via a number of distinct steps, the first being the compositional claim that water is a compound of hydrogen and oxygen. Eighteenth-century chemists did not content themselves with giving hypothetical explanations of water’s behaviour in terms of its elemental composition. Rather, they took care to establish it experimentally, taking known weights of water, decomposing them into hydrogen and oxygen, weighing the separate elements to establish that their combined weights were (roughly) the same as those of the decomposed water, then recombining them, recovering close to the original weights of water. Later, in the nineteenth century, they introduced quantitative compositional formulae which represented the proportions between the constituent elements: H_2O in the case of water.⁴ Finally, although such atomist interpretations were controversial for much of the nineteenth century, the compositional formulae came to be interpreted as embodying molecular facts, at least in some cases: for water, this meant that its characteristic molecule contains two atoms of hydrogen and one of oxygen. All this should be salutary for materialist philosophers of mind who would wish to use parallels between ‘water is H_2O ’ and ‘pain is c-fibres firing’ as a guide in developing a materialist theory of the mind. Establishing that water is H_2O was a detailed process, whose first step involved the analysis of water into its proposed constituents and then a re-synthesis from them. It does not seem unreasonable to withhold one’s assent to ‘pain is c-fibres firing’ until something analogous has been achieved.

That point made, how should ‘water is H_2O ’ be construed? To survey the alternatives, we need to identify the relata (water and H_2O) and the relation between them.⁵ First consider the relata: following Paul Needham, we can treat ‘water’ and ‘ H_2O ’ as predicates, or more likely a range of predicates. We can discuss whether these predicates correspond to properties later. What does it mean to say that something is water? First note that some substance names – ‘ice’ or ‘diamond’, for instance – refer only to specific states of aggregation: the name determines whether the relevant stuff is solid, liquid or gas. Other substance names are used independently of the state of aggregation, which must be added explicitly if it is to be specified, as in ‘liquid nitrogen’ or ‘solid carbon dioxide’. ‘Water’ has a phase-neutral use, in which we may ask (for instance) how much of it there is in the solar system.⁶ A comprehensive answer will include the solid water in the polar icecaps of various planets,⁷ liquid water in their seas (perhaps only in the case of the Earth), water vapour in their atmospheres and isolated water molecules strung out in interplanetary space. In the case of hydrogen, one would have to include the large quantities present as plasma in the interior of the sun. Clearly, nothing of interest depends on whether one allows the phase-neutral scientific usage or insists on the supposed ‘ordinary language’ usage (I use scare quotes because I am highly sceptical that there *is* an ordinary language usage that is consistent enough to be said to have an

extension). From the chemists' point of view, since there is something important that all water's different states of aggregation share, it makes sense to have one name for all these forms.

Now consider 'being H₂O'. People who know little of chemistry may take this simply to be a molecular condition (something like 'being composed of H₂O molecules'), but in general a chemical formula need not convey much information at the molecular level: it may, for instance, specify just the elemental composition of a substance, which may be shared by more than one substance. The formula 'C₂H₆O', for instance, applies both to ethanol (often written CH₃CH₂OH) and dimethyl ether (sometimes written CH₃OCH₃), which are distinct compounds with very different physical and chemical properties. So, we must ask, is 'H₂O' intended to specify the molecular make-up of water, or merely its elemental composition?

Finally, we come to the relation itself. It is well known that 'A is B' bears interpretation in terms of either identity or predication. In the present case two such interpretations suggest themselves: clearly 'water' and 'H₂O' are not the same predicate, though they may correspond to the same property. A weaker interpretation involves a relation of coextension or containment between the two predicates or properties: all A is B. If a necessity operator is envisaged (and on my view, one is required), then the source of the necessity is important. On the strongest microstructural essentialist view, which I would endorse, the relationship could be put in one of two ways: (identity) to be water is to be composed of H₂O molecules; (coextension) necessarily, all samples of water are samples of stuff composed of H₂O molecules, with the necessity in question being full metaphysical necessity. Putting this all together, 'water is H₂O' could mean either (i) 'to be water is to be made up of two parts of hydrogen to one part (by equivalents) of oxygen'; (ii) 'to be water is to be composed of H₂O molecules'; (iii) 'every sample of water is made up of two parts of hydrogen to one part (by equivalents) of oxygen'; and (iv) 'every sample of water is composed of H₂O molecules'. Different versions of (iii) and (iv) also result if modal operators are appended, and if one attends to the source of such modality (see van Brakel 2000).

Even if one takes the *strongest* essentialist reading, according which to be water *is to be* H₂O, then on the only scientifically plausible reading of what it is to be H₂O, reductionism does not follow. Why? Hilary Putnam once said that the extension of 'water' is 'the set of all wholes consisting of H₂O molecules' (Putnam 1975, 224). If a 'whole' is taken to be a mereological sum, or the result of any other composition operation in which the components are assumed to survive, this is straightforwardly false according to chemistry. Being a whole that consists of H₂O molecules may well be sufficient to be a quantity of water, but it is not necessary. Pure liquid water contains other things apart from H₂O molecules: a small but significant proportion of H₂O molecules (at room temperature, about 1 in 10⁷) dissociate (or rather self-ionise) forming H₃O⁺ and OH⁻ ions:



Furthermore, H₂O molecules are polar and form hydrogen-bonded chains which are similar in structure to ice. One might regard the ionic dissociation products and chains as impurities, but the presence of these charged species is central to understanding water's electrical conductivity. Since chemists regard the electrical conductivity they measure as a property of *pure water*, it seems gratuitous for philosophers to interpret it instead as a property of an aqueous solution of water's ionic dissociation products. Looked at this way, liquid water can at best be considered to be composed of some diverse and constantly changing population of species at the molecular scale, including H₂O molecules, H₃O⁺ and OH⁻ ions and various oligomolecular species. Can we defend the claim that water is H₂O? Yes, by considering water in all its forms to be the substance brought into being by interactions among H₂O molecules (see Hendry 2006b).

One way to synthesise all this is to regard being water as a distinct property that both molecular species and macroscopic bodies of stuff can have. H_2O molecules have it merely by virtue of being H_2O molecules. Larger bodies of stuff get it by being composed of (possibly diverse) populations of molecular species of kinds which are produced when H_2O molecules interact. Given the assumption that every part of water is water, this means that molecular species (such as H_3O^+ and OH^- ions) can be water by virtue of being part of a diverse population of molecular species which is produced when H_2O molecules interact. Hence, they acquire the property of being water by association. There is nothing strange in this. If we consider the protons in water to be part of the water, they acquire their wateriness by association too.

In a less exciting sense, wateriness is therefore an emergent property because nothing below a particular size (that of an H_2O molecule) can be water on its own account, and some smaller fragments acquire the property by association.⁸ But that doesn't tell us whether being water is a *strongly* emergent property, that is, whether or not being water confers additional causal powers. This is where the standard argument I mentioned earlier comes in, except we can now see that it runs into difficulty. Consider all the different kinds of thing that, we have agreed, count as quantities of water, from mereological sums of water molecules to steam, liquid water and (the various forms of) ice. Trivially, a mereological sum of water molecules is no more than the sum of its parts. Any powers it has are acquired from its constituent H_2O molecules. But it has no bulk properties, so there is no distinction to be made between its molecular and its bulk properties. Steam, liquid water and (the various forms of) ice do have bulk properties, each bearing distinct sets of properties produced by the distinct kinds of interactions between their parts. Wherever there is significant interaction between the H_2O molecules, there is scope for that interaction to bring new powers into being. This is particularly obvious if that interaction includes self-ionisation and the formation of oligomers: the excess charge of solvated protons can be transported across a body of liquid water without the transport of any matter to carry it, via what is called the Grotthuss mechanism. This, in fact, is why water conducts electricity so well, unlike other, similar hydrides. The power to conduct electricity is not possessed by any sum of (neutral) H_2O molecules. The mechanism by which that power is exercised requires some part of the molecular population to be charged. It therefore depends on a feature of a diverse *population* of molecular species.

The reductionist will say at this point that the water can only acquire its causal powers from its parts and interactions between them. So, no novel causal powers have been introduced. The strong emergentist will ask why, when it is being decided whether they are novel, the powers acquired only when the molecules interact are already accounted for by the powers of H_2O molecules. If the rule is that any power possessed by any molecular population produced by any interaction between H_2O molecules is included, and we know this rule to apply independently of any empirical information we might ever acquire about what water can do and how it does it, then it seems that we know *a priori* that there will be no novel causal powers. The strong emergentist is within her rights to insist on a good scientific argument for this claim before accepting it into the debate. This does not, of course, mean that the strong emergentist wins the argument by default: only that in the absence of a specific *scientific* argument, the reductionist and the strong emergentist conclude this discussion honours even. Anti-reductionists need not fear theoretical identities, and should even learn to love them.

Structure and scale

Structure is central to chemistry: substances are named and classified by chemists in ways that depend entirely on their structure at the molecular scale, and structure grounds our understanding of their chemical reactivity and spectroscopic behaviour. In an important sense, the identity of a substance depends on its structure at the molecular scale (Hendry 2016a).

To say that a chemical substance has a ‘structure’ at the molecular scale might suggest to some philosophers that physical forces hold atoms and ions in static relative spatial positions. This may be why the term ‘arrangement’ has such currency in debates between philosophers concerning the metaphysics of composition (see for instance van Inwagen 1990; Sider 2013). However, objects at the molecular scale *cannot* be static because of zero-point motion: a minimal random motion associated with the lowest possible energy state of a quantum-mechanical system. A proper understanding of structure at the molecular scale must be consistent with the fact that atoms and ions are always in motion, even at absolute zero. Above absolute zero one must add thermal fluctuations: if the parts of a structure exhibit relative positions, such as the sodium and chloride ions in the lattice of common salt, these must be equilibrium positions, around which the various parts move, like a pendulum bob. Motion in a physical system depends on the energy it contains, so the ionic motions in a salt lattice will increase as its temperature increases (until, of course, the lattice breaks down). This dependence means that the structure of an ionic lattice is relative to temperature, and therefore energy (for a more extended discussion of all these points see Hendry forthcoming).

A well-known discussion of ice provides another example of the scale-relativity of lattice structure. Eisenberg and Kauzmann (1969, 150–152) point out that H₂O molecules in ice undergo vibrational, rotational and translational motions, with the molecules vibrating much faster than they rotate or move through the lattice. At very short timescales (shorter than the period of vibration), the structure of ice is a snapshot of molecules caught in mid-vibration. It will be disordered because different molecules will be caught in slightly different stages of the vibration. As timescales get longer, the structure averages over the vibrational motions and then (at yet longer scales) the rotational and translational motions. This yields successively more regular but diffuse structures. Therefore

the term ‘structure’ can have three different meanings when applied to a crystal such as ice. The meaning depends on whether one considers a time interval short compared to the period for an oscillation (τ_v), or an interval longer than the period of an oscillation but less than the time for a displacement (τ_D), or an interval considerably longer than the displacement time.

(1969, 151)

Chemists describe organic substances in terms of what I have called bond structure, which is distinct from the kind of structure exhibited by such ionic lattices as solid sodium chloride (see Hendry 2016b). This slightly complicates matters. Consider ethane (C₂H₆), in which a single bond links two carbon atoms whose remaining valences are used up by six hydrogen atoms. The geometry of the carbon atoms is roughly tetrahedral, the H–C–H angle being around 109 degrees. Further geometrical details of the ethane molecule are complicated by the fact that the two methyl groups rotate quite freely around the single bond between the two carbon atoms. Given the bond angles between the hydrogens attached to each carbon atom, one can distinguish two different geometrical configurations (or conformations) that ethane can take: staggered ethane, in which the hydrogen atoms are offset, and eclipsed ethane, in which they are aligned. These two different conformations can be represented by Newman and sawhorse projections, as in Figure 27.1.

The staggered conformation is of slightly lower energy than the eclipsed conformation, so rotation around the C–C bond is not entirely free. Nevertheless ethane, as Bassindale colourfully puts it, ‘can be thought of in terms of two linked CH₃ propellers, with each CH₃ rotating rapidly’ (1984, 25), and the eclipsed conformation now appearing as three small regularly occurring

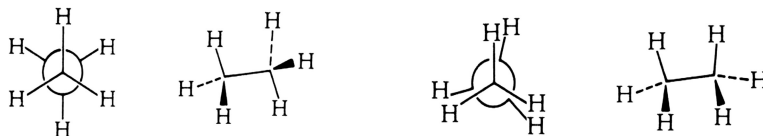


Figure 27.1 Newman and sawhorse projections of staggered ethane and eclipsed ethane, from Bassindale 1984, 50. Staggered ethane is represented by the two projections on the left, eclipsed ethane by the two on the right.

hindrances, passed over by the propellers like bumps in the road. Because ethane is always in motion, it presents distinct geometrical structures at different timescales: according to Bassindale ‘measurement techniques with relatively long timescales would show an averaged geometry for ethane, but very short-timescale techniques could observe ethane in a staggered conformation’ (1984, 51). Ethane’s bond structure is an invariant feature throughout these motions. It is a complex structural property in common to all the different conformations.⁹

A substance may also present distinct structures at different length scales. Seen from afar, a steel bar looks homogeneous, with homogeneity being a null kind of structure. Closer in, there are imperfections: discontinuities giving rise to a grain structure at the millimetre scale. Within the grains are atomic lattices. These differences of structure across scales are reflected in physical explanations of steel’s behaviour at the various scales (see Batterman 2013).

This suggests that chemical substances and other materials cannot be said to have a single structure, instead exhibiting a variety of them, each emerging at different scales of length, time and energy. It may be tempting to privilege the structures presented at close range, and at shorter timescales, over those which are observed at long range and longer timescales. One might even doubt that the longer-range and timescale structures are really distinct at all if they are just dim impressions of, or averages over, the close-range or short-timescale structures. If one takes a series of snapshots at a higher frequency, one could reconstruct the average one would see at a lower frequency.¹⁰ Yet there is a counterfactual difference: many different series of snapshots could have given rise to the same average, and which particular series was seen is irrelevant. Put another way, the averaged picture is what one sees at the particular frequency that is appropriate to it. In a slightly different context (a discussion of boundaries), Achille Varzi goes a step further than reduction, arguing that a boundary seen from afar must be illusory, because it disappears on closer approach:

It is true that I had the impression of seeing the shoreline of Long Island from my plane; but it is also true that when you actually go there, ground-level, things look very different. What looked from the air like a sharp line turns out to be an intricate array of stones, sand, algae, piers, boardwalks, concrete blocks, musk sediments, marshy spots, putrid waters, decayed fish.

(2011, 139)

Moreover if a coastline is identified with the ‘water/sand interface’, ‘[t]hat boundary is constantly in flux, and it is only by filtering it through our cognitive apparatus – it is only by interpolating objects and concepts – that a clear-cut line will emerge’ (2011, 139). I don’t think one should dismiss the lower-resolution views. Even if the straightness disappears when one gets closer, a beach that looks long and straight from the air *really does* present a long straight boundary to incoming water waves, producing plane waves by reflection. Concentrating only on the view from close up, one may literally lose this bigger picture. The shape of the beach, like the structure

of a molecule, depends on the scale at which one is considering it. The correct scale may not be a choice, but is fixed for us by some salient process, such as the formation of water waves (for the beach) or interaction with radiation (for molecules). These are matters of physical interaction, not of perception or conception.

A second aspect of the scale relativity of structure is that relationships of structural sameness and difference vary across different scales. This variation can occur at two different levels: in the way that molecules interact to form macroscopic substances and in the structural distinctness of the molecules themselves. At the level of the substances, consider Louis Pasteur's achievement in separating by hand crystals of the L- and D-forms of sodium ammonium tartrate, obtained from a racemic solution (an equal mixture of the two). This is a famous exemplar of structural explanation in science, and its experimental demonstration for the L- and D-forms are enantiomers: structures which are mirror images but which cannot be superimposed on each other. It is less well known that had Pasteur attempted the separation at a higher temperature than he did, he would likely have failed, because above 26°C the L- and D-salts form a single racemic crystal (Kauffman and Myers 1975).¹¹ How the two different species aggregate to form macroscopic crystals depends on temperature: it is a scale-dependent process.

For an example of the timescale dependence of structural sameness and difference in a single molecule, consider substituted biphenyls, which contain pairs of benzene rings connected by a single bond (see Figure 27.2).

When the hydrogen atoms in the benzene rings are substituted by functional groups X and Y in the four positions shown, the possibility of a new form of stereoisomerism arises – the molecule can in principle exist in two enantiomeric forms – but the isomerism is interestingly temperature dependent. In general, single carbon–carbon bonds, like the one connecting the two benzene rings, allow free rotation of the groups they connect. If the groups X and Y are relatively small (e.g. single atoms such as hydrogen or fluorine), then that rotation will be relatively unrestricted, though there will be some steric hindrance: groups X and Y will bump past each other, like the hydrogens in ethane. In such cases the two enantiomers will not be separable at room temperature because they will interconvert. There are not two enantiomers, just two enantiomeric conformations of a single structure. For larger X and Y, perhaps the enantiomers can be separated, but they racemize rapidly. For really bulky groups such as $-\text{NO}_2$, or $-\text{COOH}$, the interaction between them will constitute a barrier to the rotation – the two enantiomers will be separable and will racemize only slowly. So for any given substituent groups X and Y, the physical distinctness of the enantiomers disappears above a characteristic temperature. Hence, the structural sameness and difference of molecular species is also a temperature-dependent (and therefore energy-dependent) phenomenon. The structures of molecules are dynamic configurations which are 'frozen in' at the particular energy scales at which they can exist. Each biphenyl enantiomer breaks the underlying symmetry of the situation, a symmetry which, as we have seen, reasserts itself sooner or later.

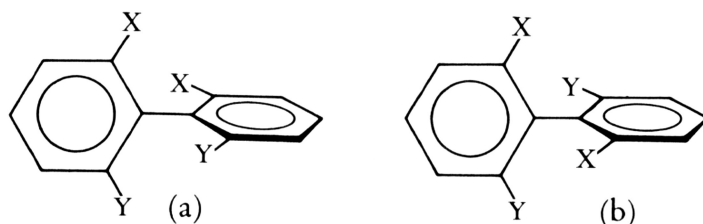


Figure 27.2 Biphenyl atropisomers, from Bassindale 1984, 58.

The idea that structure is frozen in when a system lacks energy could be applied to the whole of chemistry, which studies states of matter whose behaviour is dominated by the particular kinds of interactions that occur between atoms and ions: nuclei which are at low enough temperatures to have captured electrons and exhibit the stable electronic structures which give rise to the formation of chemical bonds. Once we go beyond the energy scales at which stable atoms and ions can exist, chemistry as we know it ceases to happen.

Emergence of molecular structure

A detailed examination of how molecular structures are explained within quantum mechanics puts pressure on the idea that they can be said to be derived from the basic laws of that theory. Quantum mechanics describes many-body systems of electrons and nuclei in terms of the Schrödinger equation, whose solutions correspond to the possible stationary states of the system. Electronic and nuclear motions are first separated, on account of the very different rates at which they move, and respond to external interactions. This is the adiabatic approximation, which yields wavefunctions for two coupled systems (of electrons and of nuclei), dynamically evolving in lockstep. When modelling a molecular structure, the nuclei are then typically localised, corresponding to the equilibrium positions of the known structure. Density-functional theory (DFT) replaces the 3N-dimensional electronic wavefunction with a three-dimensional electron density function (it can be shown that this can be done without approximation). According to the Hellmann-Feynman theorem, the overall force on a nucleus in the system is determined by the electron density, so effectively the nuclei are being pushed around by their interactions with the electrons.¹² The structure is then explained by showing that it corresponds to a configuration in which the energy is a minimum (i.e. the forces on the nuclei are effectively zero).

Two things are worth noting. Firstly isomers, which are molecules in which the same types of atoms are bonded together in different ways, share their molecular Schrödinger equations, the starting point of the earlier explanation. Thus, ethanol $\text{CH}_3\text{CH}_2\text{OH}$ and dimethyl ether (CH_3OCH_3) share the same Schrödinger equations, as do enantiomers such as L- and D-tartaric acid (see Sutcliffe and Woolley 2012). The starting point of the explanation, the molecular Schrödinger equation, does not respect the differences between isomers. What results from localising the nuclei *does* respect these differences. Hence, in localising the nuclei in positions which correspond to the different isomers, these differences are being put in by hand. Thus, the different structures, their different symmetry properties and the different causal powers they ground are effectively introduced as unexplained explainers. As noted, the reductionist will see this as a pragmatic move: we cannot directly solve the molecular Schrödinger equations and so must introduce approximations whose results should not be seen as having any independent explanatory power. But it is hard to see these moves as mere approximations because they so radically transform the physics of the problem. This transformation is not a mere approximation since it transforms the scope of the equation, and it seems hard to argue that the approximations have no independent explanatory power. The molecular structures could not, *in principle*, appear without them.

A second point concerns how physical approximations work. The reductionist assumes that they have no independent explanatory power, because they are proxies for the exact equations: anything that could be explained using an approximate model could be explained using the exact equations. This would be a reasonable thing to conclude if the conditions which define the model could be derived from the exact equations or shown to be metaphysically unimportant in some way. One might, for instance, regard the necessary conditions merely as initial or boundary conditions and no more interesting than the 'auxiliary assumptions' that generate the Duhem-Quine problem. The story goes like this: quantum mechanics (QM) implies the existence of

molecular structure (MS) only in conjunction with statements describing the necessary boundary and initial conditions (BIC). Thus, QM and BIC imply MS. This is all correct: adiabaticity and nuclear localisation might plausibly be thought of as boundary conditions, while the choice of nuclear positions looks like an initial condition. But this is no help to the reductionist who wants to see this explanation as a derivation from quantum mechanics, because as we have noted, exactly meeting the adiabaticity and nuclear localisation conditions is impossible for any quantum system. Thus, the conjunction of QM and BIC is, in some important sense, incoherent.

It is less misleading to put the point as follows: the mathematics provides only what one might call a *dynamical consistency proof*: the conditions which define the model *could not* hold exactly in any situation in which the exact equations hold,¹³ but the two kinds of systems will evolve dynamically in approximately similar ways for some given level of accuracy and over the timescales relevant to the calculation. As we have seen, the molecular structure calculations described earlier assume dynamical conditions – the adiabatic separability of electronic and nuclear motions and the localisation of the nuclei – which *could not* hold exactly in any quantum system. All that can be assumed therefore is that a quantum-mechanical system of electrons and nuclei will display approximately similar dynamics to the model. No derivation of the model dynamics from the exact equations has been provided, nor even a demonstration of their logical consistency. All that the mathematics provides is that approximations introduced in the model can be neglected for a given level of accuracy over relevant timescales.

In joint work with Robert Schoonmaker (Hendry and Schoonmaker forthcoming), rather than treating adiabatic separability and nuclear localisation as mere approximations, we interpret them as substantive special assumptions about dynamical interactions within a many-body system of electrons and nuclei. If it can be shown that these conditions are necessary for molecular structure, the emergentist will regard them as necessary conditions for molecular structure itself to emerge (for the moment, I leave aside the question of whether these conditions are sufficient for the emergence of molecular structure).

As already noted, these conditions radically transform the dynamical behaviour of quantum systems and the scope of the equations that describe them. Adiabatic separability makes the overall energy of the electrons and nuclei a function of the nuclear configuration so that the dependence of energy on nuclear positions can be mapped by a potential energy (PE) surface (or rather as a hypersurface). This is not a global assumption (it depends on adiabatic separability), and a system of electrons and nuclei will not have a global PE surface: PE surfaces are not foliated, and near where they cross, the adiabatic separability of nuclear and electronic motions breaks down (see Lewars 2011, chapter 2). The effect of nuclear localisation is just as radical and interesting, for it suppresses quantum statistics. In general, any quantum system of electrons and nuclei must obey nuclear permutation symmetries: the overall wavefunction must be symmetric (for bosons) or antisymmetric (for fermions). In a quantum system with a molecular structure, the nuclei can be localised by their interaction with the electrons (whose joint quantum-mechanical state also reflects their interactions with the other nuclei) so that it makes a negligible difference to the dynamical evolution of the system whose statistics is assumed to apply: whether the overall wavefunction is symmetric (Bose–Einstein statistics), antisymmetric (Fermi–Dirac statistics) or indeed *asymmetric* (classical statistics) with respect to nuclear permutation. Interaction with the rest of the system effectively transforms the nuclei from quantum entities into classical objects. It should be emphasised that neither of these conditions is necessary for bonding as such: condensed matter physicists study systems such as metals and superconductors in which there is bonding (since they form cohesive materials), but in which nuclear and electronic motions are not adiabatically separable, and in which the nuclei are not localised, in the sense that quantum statistics must be taken into account in describing their structure. These conditions are necessary only for

the kind of structure that is describable in terms of the classical chemical structures developed in organic chemistry during the nineteenth century. Interestingly there are molecules, such as protonated methane, in which some of the nuclei are localised but others are not. The permutation symmetries of two non-localised protons in protonated methane are therefore expressed in the dynamical behaviour of the molecule (see Hendry and Schoonmaker forthcoming).

These two conditions – adiabatic separability of nuclear and electronic motions and nuclear localisation – are not, however, sufficient for the emergence of classical molecular structure. Some molecules, such as cyclobutadiene, tunnel between two different structures, each of which is expressed in the molecule's interaction with radiation: in infrared (IR) spectra the molecule exhibits square symmetry, while higher-frequency x-ray diffraction catches it in the rectangular states between which it tunnels (see Schoonmaker, Lancaster and Clark 2018). This is another expression of the scale relativity of structure. It should be emphasised that tunnelling between different structures is the normal quantum-mechanical behaviour, but the dynamical behaviour of many molecules can be understood in terms of a single classical structure. Hence, dynamical restriction to a single structure is a third necessary condition for the classical kind of structure that is exhibited by many organic molecules.

Conclusion

In this chapter I have explored the positive reasons that chemistry provides to see substances and their structures as emergent. There were three levels of emergence: how substance properties, and substances themselves, emerge from the diverse populations of molecular species which compose them; how the structures of molecular species emerges in a scale-relative manner from their characteristic motions; and how the emergence of molecular structure requires three necessary conditions governing dynamical interactions between electrons and nuclei. Each case exemplifies a characteristic feature of emergence: that the existence of the emergent requires distinct kinds of cooperation and organisation between its parts.

Too often, scientists and philosophers approach relationships between physics and the special sciences via 'one-size-fits-all' interpretations, including various kinds of ontological reductionism combined with instrumentalist interpretations of the special sciences, according to which they provide no more than useful fictions that stand in proxy for the computationally intractable fundamental equations of physics. These approaches are inadequate in so many ways. They are insensitive to the important differences between the various special sciences, one especially salient distinction being that between sciences which are commensurable with physics (such as chemistry and condensed matter physics) and those which are not, because they involve function or teleology (such as biology and psychology). They can also be epistemically closed to evidence against them, like conspiracy theories. To everything I have said, the ontological reductionist can respond, quite correctly, that it is all perfectly consistent with the ontological reducibility of chemistry. The solipsist can make the same response to the evidence of their senses. A better understanding of the situation requires us to weigh the evidence *for* ontological reducibility, as against weaker kinds of dependence.

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Notes

- 1 Reductionists should also accept the possibility that non-derivability reflects a need to revise currently accepted physical principles.
- 2 Linus Pauling took just this view of quantum chemistry (see Hendry 2012).
- 3 An issue also discussed by Joseph LaPorte (2004) and Michela Massimi (2012).
- 4 Note that the proportions were not between the weights of the elements, but between equivalents; thus, 'water is H₂O' represents the fact that it contains twice as many equivalents of hydrogen as of oxygen, although the oxygen-hydrogen weight ratio in water is more like 8:1.
- 5 In the following discussion I am indebted in many ways to Paul Needham (2000, and many conversations), although we are in clear disagreement on some of the issues.
- 6 Note that various chemical processes produce and consume water. Hence, the total amount of water in the solar system will vary, so the question must be asked with reference to some period of time.
- 7 In fact John Finney (2004) identifies 16 distinct structures for ice, which form under different thermodynamic conditions.
- 8 In case the claim that 'every part of water is water' sounds odd, consider that there is nothing in pure water that isn't water. It may become more acceptable if one considers chemical substances to be modes in the medieval sense: ways that matter can be. All the parts of a pure sample of water are acting together to be water. Wateriness is a property that matter may acquire and lose. I am grateful to Alisa Bokulich for pressing me on this point.
- 9 For the distinction between bond structure (which the different conformations share) and geometrical structure (with respect to which they differ), see Hendry (2016b), where I also argue that neither kind of structure is more fundamental than the other kind.
- 10 I am grateful to Robert Schoonmaker for helpful discussion on these points.
- 11 I am grateful to John Hudson for this reference.
- 12 Although note that, since DFT folds interactions with other nuclei into the electron density, each of the nuclei is really being pushed around by its interactions with the rest of the system.
- 13 In a similar fashion, under the assumption that the sun has a finite inertial mass, no Newtonian solar system could display Keplerian orbits. Nevertheless, astronomers down the ages have chosen planetary orbits from among the conic sections, which assume that the sun is at rest.

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