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Chapter 8

A Commentary on Robin Hendry's Views on Molecular Structure, Emergence and Chemical Bonding



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Abstract In this article I examine several related views expressed by Robin Hendry concerning molecular structure, emergence and chemical bonding. There is a long-standing problem in the philosophy of chemistry arising from the fact that molecular structure cannot be strictly derived from quantum mechanics. Two or more compounds which share a molecular formula, but which differ with respect to their structures, have identical Hamiltonian operators within the quantum mechanical formalism. As a consequence, the properties of all such isomers yield precisely the same calculated quantities such as their energies, dipole moments etc. The only means through which the difference between the isomers can be recovered is to build their structures into the quantum mechanical calculations, something that is carried out by the application of the Born-Oppenheimer approximation. Consequently, it has been argued by many authors that molecular structure is written in 'by hand' rather than derived. Robin Hendry is one such author, but he goes a great deal further by proposing that this situation implies the existence of emergence and downward causation. In the current article I argue that there are alternative explanations which render emergence and downward causation redundant. Such an alternative lies in the notion of quantum decoherence and the appeal to work in the foundations of physics, which posits that the various isomers exist as a superposition until their wavefunctions are collapsed either by observation or by interacting with their environment.

Hendry also alludes to a debate among chemists as to whether chemical bonds are real or not, in the sense of directional connections between two or more nuclei in any given molecule. I reject this view and propose that the structural and energetic views of chemical bonding, that have been discussed by some philosophers of chemistry including Hendry, do not refer to any essential ontological differences. I agree that chemists view bonding in a more realistic fashion and may consider bonds to be in some senses real, while physicists may consider bonding in more abstract energetic terms. However, I do not believe that such differences in scientific practice and attitudes should be considered to offer a window as to the ontological

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status of bonding or whether bonding is real. Finally, I discuss the kinetic energy school of chemical bonding which would seem to challenge any notion of bonds as directional entities, since bonding is no longer regarded as being primarily due to the build-up of electron density between nuclei.

Keywords Emergence · Reduction · Born-Oppenheimer · Causation · Molecular structure · Bonding

8.1 Introduction

Over a period of many years Robin Hendry has proposed a number of related views on the philosophy of chemistry. In the present article I intend to examine some of these views in detail. Like many other philosophers of chemistry before him, Hendry has worked on the question of molecular structure and its relationship with quantum mechanics.¹ Molecular structure is of course a central and important concept in chemistry with an enormous amount of experimental evidence to support its existence. Similarly, quantum mechanics represents a major pillar of modern physics and a dominant paradigm for the study of radiation and matter, which has yet to be refuted after about 100 years since it was first developed.²

The problem lies in trying to connect molecular structure with quantum mechanics. To cite a common example that is discussed in the literature, a pair of isomers, such as C_2H_5OH (ethanol) and CH_3OCH_3 (dimethyl ether) have different molecular structures even though they share precisely the same Hamiltonian operator within their quantum mechanical description.

When the Hamiltonian operates on the wavefunction for these molecules it therefore yields precisely the same energy, as well as any other properties that one may care to extract from such computations. Briefly put, quantum mechanics appears to be incapable of distinguishing between two such isomers unless one important further step is taken, namely the introduction of the so-called Born-Oppenheimer approximation. This procedure corresponds to assuming that the positions of all the nuclei in a molecule are stationary, relative to the movement of their far lighter electrons.

As a result of this approach the act of solving the Schrödinger equation for these molecules is simplified considerably. In other words, the structure of the molecule, as defined by the positions of the nuclei, is written into solution of the problem from the outset. Quantum mechanics does not therefore derive the structure of the molecule since one assumes it from the start.

This situation is somewhat analogous to that of the old quantum theory in the early years of the twentieth century. The Bohr model was successful at describing

¹Primas (1983), Woolley (1976).

²Histories of quantum theory and the later quantum mechanics include Jammer (1966) and Mehra and Rechenberg (1987).

one-electron systems but the quantization condition for the energy of the electrons had to be written into the treatment from the beginning. Stated otherwise, quantization was assumed rather than being derived. As I see it, a similar situation exists in the molecular structure problem, in which structure is typically assumed rather than being derived.

If my proposed analogy has any validity, one may wonder whether future developments in quantum mechanics might not resolve the molecular structure issue and render structure derivable.³ So far, the story I have sketched is well known and has been addressed by many authors from different perspectives (Primas, 1983; Woolley, 1976).

What Hendry brings to this issue is the view that this 'gap' between molecular structure and quantum mechanics should be interpreted as indicating that molecular structure 'emerges' in some sense. Furthermore, Hendry proposes that we should think of two kinds of molecular Hamiltonians. First of all, he speaks of the true, or resultant, Hamiltonian which does not help itself to the Born-Oppenheimer approximation, meaning that molecular structure is not assumed from the outset. He then proceeds to contrast this form with a Hamiltonian that does make use of the B-O approximation, in which the nuclear positions are fixed and which he terms the configurational Hamiltonian. Hendry also accompanies this proposal with the radical claim for the existence of downward causation, through which molecular goings on can somehow influence their component particles.

Let us return for now to the notion of emergence. Hendry has claimed that according to the current state of quantum chemistry, there is at least as much evidence for emergence as there is for the ontological reduction of chemistry, but concludes by favoring emergence. This claim would seem to be rather extravagant, at least to the present author as I have argued in more detail in a previous publication (Scerri, 2012).⁴

8.2 On Epistemological and Ontological Reduction

Hendry quite correctly contends that quantum mechanical theory is abstract, whereas any particular situation is highly specific and necessitates the use of approximations. It is possible, he continues, that any failure of reduction can be

³One possible candidate for such a development has already been outlined by Sir Roger Penrose who believes that gravity modifies quantum mechanics in a profound manner which, among other things, may provide a natural explanation for what happens during the collapse of the wavefunction (Zurek, 2003).

⁴In any case, the burden of proof lies with those who claim the existence of emergence, rather than for critics to have to provide detailed counter arguments as to why it does not even exist. Emergence may well be a buzz word in the philosophy of science literature but there is no agreement as to how it can be characterized. It certainly has no traction among the vast majority of working scientists with the exception of some cosmologists who have argued that space-time somehow 'emerges' from more fundamental quantum levels or reality (Gambini & Pullin, 2020).

attributed to making such approximations. If so, then a reduction would have failed on epistemological or inter-theoretical grounds. One cannot conclude, Hendry argues, that there is a lack of ontological reduction. So far, I am in complete agreement.

Hendry also points out that a pair of disciplines, such as chemistry and physics, typically develop independently as history unfolds and that there is no guarantee that the two sciences should mesh together perfectly in such a way that reduction could ever be established. If this is the case, then once again any apparent lack of reduction can be attributed to inter-theoretical issues and one cannot rule out the ontological reduction of one level to another one.

However, the failure of reductionism on these sorts of grounds cannot be conclusive when it comes to the more general question of ontological reduction. In order to articulate a form of ontological reduction, we need to look elsewhere. Hendry then turns to the more difficult task of venturing an opinion concerning ontological reduction,

if the reduction debate is to develop beyond the impasse over inter-theoretic reduction, it must turn to the ontological relationships between the entities, processes, and laws studied by different sciences, which are fallibly and provisionally described by their theories. One obvious requirement on 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, p. 184).

This is an important point that, as I believe, Hendry fails to embrace fully when he addresses the issue in more detail. Moreover, I suggest that it is rather difficult to give arguments that transcend our current explanatory schemes and theories. As I see it, Hendry and other authors who claim to separate ontological question from inter-theoretical questions by focusing on entities rather than theories, may be mistaken.

Hendry continues,

reducibility is at the strong end of the spectrum because it is the limiting case that denies the distinct existence of what is dependent—the reductionists slogan is that x is reducible to y just in case x is ‘nothing but’ its reduction base, y . One can imagine many ways to cash out this slogan, depending on the aspect under which the reduced is held to be ‘nothing but’ its reduction base, but a consensus has emerged in recent philosophy of mind that the relevant aspect should be causal. Alexander’s dictum is the principle, often cited by Kim (1998, p. 119, 2005, p. 159), according to which being real requires having causal powers (Hendry 2010, p. 184).

This appears to represent a major pivot which deserves more scrutiny, namely the connection between the question of causation and that of reduction. First of all, the fact that a consensus may have arisen in the philosophy of mind may not be relevant to research in the philosophy of chemistry. Why after all should one accept a consensus that may have emerged in a completely different branch of philosophy? Moreover, the importance of causation is far from universally accepted in the philosophy of science and indeed there is a growing belief among philosophers of physics, and others, that not all explanations are necessarily of a causal nature (Norton, 2003; Lange, 2013). In addition, some theoretical chemists have also

recently denied the notion that causation plays any role whatsoever in the domain of chemistry (Matta, 2023).

The re-appearance of causes in the philosophy of science, after they had been abolished by the Logical Positivists, is a complicated issue whose examination would take us too far afield and will not be considered here (Scerri, 2021). Suffice it to say that the symmetry between explanation and derivation which existed in the logical positivist account of science became threatened because of some cases which represented a derivation while it appeared as though there was no explanation.

The classic instance of this kind is one concerning a flagpole and the shadow that it casts on a sunny day. One can calculate the length of the shadow from the height of the pole and a little trigonometry. Conversely one can calculate the height of the pole from the length of the shadow. However, one would not want to claim that the length of the shadow somehow causes the height of the flagpole. Causation seems to operate in only one direction. Examples of this kind convinced philosophers of science of the need to reintroduce the notion of causation into the philosophy of science. Since causation is not symmetrical, in the same way that derivation is, the causal direction needs to be included into any account of explanation, or so the post-Positivist story goes.

But more recent work, as already mentioned, has questioned the contemporary hegemony of causal explanations, particularly in the most fundamental discipline of physics (Rivadulla, 2019). But let us assume, for the sake of the present discussion, that there is indeed a strong connection between causation and reduction in the way that Hendry assumes when he writes,

the ontological reductionist thinks that special-science properties are no more than their physical bases because the causal powers they confer are a subset of those conferred by their physical bases; the emergentist sees them as distinct and non-reducible just because the causal powers they confer are not exhausted by those conferred by their physical bases. The additional causal powers are exerted in downward causation (Hendry 2010, p. 185)

Hendry then appeals to the work of C. D. Broad on emergentism and claims that it provides an account of emergence from which a model of downward causation is easily extracted. Writing in the 1920s Broad made a contrast between what he called 'pure mechanism' whereby every material object is made of fundamental particles of one kind of stuff and emergentism where this is not the case. Moreover, according to Broad, one physical law governs the interaction between the particles, and according to pure mechanism, this law determines the behavior of every material object. Hendry's gloss on this point is,

Broad's account of the disagreement between pure mechanism and emergentism is easily formulated within quantum mechanics, in which the motions are governed by Hamiltonian operators determined by the forces acting within a system (Hendry 2010 p. 184).

The notion that such a connection between emergentism and quantum mechanics may be easily formulated also seems rather extravagant. Countless attempts to settle such questions within the philosophy of physics have been highly inconclusive and far from easy. It is by no means clear whether reductionism breaks down in the domain of quantum mechanics.

Hendry also claims that whereas the reductionist posits a resultant Hamiltonian, the emergentist posits a non-resultant Hamiltonian or “configurational Hamiltonian” but unfortunately is unable to identify any such configurational Hamiltonians for the examples which he discusses.

So far, I have largely been summarizing an article which I published in 2012 but which Hendry has yet to respond to (Scerri, 2012). In the same article I suggested that a different alternative, to the existence of emergence, might be to consider the notion that the isomers of any compound, such as one possessing the molecular formula $C_2H_6O_1$, when first formed, might consist of a superposition of its possible isomers. After a very brief period of time the now well accepted process of quantum decoherence might occur so as to collapse the superposition into an actuality featuring one specific isomer. Said in different words, I proposed that at the most fundamental level the initial formation of a molecule really does lack a structure in the sense that it has not yet actualized into a particular structural isomer.

This appeal to the work in the foundations of physics and the question of the collapse of the wave function has been rendered more attractive by the realization that the collapse of the wavefunction can even occur in the absence of observation. All that is required is for there to be an interaction with the environment in which the molecule finds itself in. For example, something as small as a grain of dust is now known to be capable of collapsing the wavefunction (Zurek, 2003). Moreover, research into the foundations of physics has made it possible to compute the decoherence time for any particular molecule, which is typically of the order of femtoseconds. What this amounts to, is the plausible scenario whereby a molecule initially forms as a result of a particular reaction, say the synthesis of $C_2H_6O_1$ and after such a very brief passage of time has elapsed, just one of the two possible structural isomers comes into being.⁵

My proposal for considering the question of the collapse of the wavefunction and quantum decoherence has now been picked up by Seifert and Franklin who have developed a far more detailed account than I could ever have done, as a means to counter any claims as to the occurrence of emergence (Franklin & Seifert, 2023).

8.3 Bonding

The second major theme in the work of Hendry that will be considered is his view of chemical bonding. In previous publications I have suggested that chemical bonding is one of the two big ideas in chemistry, in response to some philosophers of physics who deny any form of philosophical importance to the field of chemistry (Scerri, 2020). Molecular structure and bonding are among the most quintessential topics that have been considered by the new wave of philosophers of chemistry that

⁵ In general, the superposition may involve any number of structural isomers which share the same molecular formula.

began to take shape in the mid 1990s. It is therefore essential that such views be subjected to careful consideration.

The topic of chemical bonding has a long and complicated history, which can be taken to begin with the work of chemist John Dalton at the beginning of the nineteenth century. Dalton revived the atomic theory of the ancient Greek philosophers, some of whom held that matter is not infinitely sub-divisible, but that a limit is reached once one arrives at the atoms, that are the smallest components of each of the elements (Greenaway, 1966).

Dalton proceeded to consider the combination of atoms to form molecules such as water, which he incorrectly believed to consist of one atom of hydrogen combined to one atom of oxygen. The nature of the attraction between these two kinds of atoms was a source of great difficulty for early chemists such as Dalton. In some respects the mystery remains up to the present time, although very accurate calculations on the properties of molecules can now be carried out.

Nevertheless, the question of what chemical bonds actually consist of continues to pose problems and there are many remaining disagreements among professional chemists (Malrieu et al., 2007; Rzepa, 2009).

One of the earliest views that was contemplated was that chemical bonds are physical links between the constituent atoms. These physical connections were thought to be stick like linkages or perhaps in the form of mechanical springs. Stated otherwise, bonding was originally viewed in a naïvely realistic sense of physical entities which were as substantial as the atoms that they were thought to connect together.⁶

In the early part of the twentieth century great advances were made, resulting in the classification of chemical bonds into the categories of ionic and covalent bonding. Ionic bonding was postulated first to consist of an attraction between charged ions, resulting from the complete transfer of electrons from metal atoms to atoms of non-metals. The ions formed in this way were considered to attract each other and to form three-dimensional crystal lattices, such as in the classic example of sodium chloride (Kossell, 1916). Soon afterwards an alternative form of bonding was proposed by G.N. Lewis, in order to explain the existence of non-polar compounds, in which oppositely charged ions did not play any role (Lewis, 1916). This other major form of bonding was called covalent bonding in order to reflect the notion that constituent atoms were sharing electrons rather than transferring them. Examples include such molecules as diatomic gases such as H₂, O₂ and so on. For about 100 years schoolchildren have been learning the basic distinction between these two kinds of chemical bonds right from the beginning of their chemistry courses.

As in the case of most elementary ideas in science, this simple picture must be qualified as instruction in the subject is taken to more advanced levels. For example, one must appreciate the fact that the two forms of bonding are but extremes on a single continuous spectrum. It is more helpful to think of the two forms of bonding

⁶To the extent that atoms were regarded as real physical entities, a view that was by no means universal among chemists such as Mendeleev and many others, especially in the eighteenth and nineteenth centuries.

as being cases of approximately equal sharing of electrons in the case of covalent bonding, as compared with very unequal sharing of electrons in the ionic case.⁷ Any philosophical analysis which is predicated on the characteristic difference between ionic and covalent bonding is therefore problematical from the outset, a feature which I believe has occurred in some of the recent discussion in the philosophy of chemistry community, as I will attempt to explain.

8.4 Hendry's Contrast Between the Energetic and the Structural View of Bonding

In a further series of articles Robin Hendry has written about what he considers to be opposing views concerning the nature of chemical bonding. Hendry's 'structural conception' of chemical bonding consists of the claim that a covalent bond is a directional, sub-molecular relationship between individual atomic centers, that is responsible for holding the atoms together. However, even in classical chemistry covalent bonding is not invariably directional and it is not necessarily sub-molecular, although I will delay a fuller discussion of these points for the moment.

It is well-known that the distinction between ionic and covalent bonding is something of an over-simplification. The modern study of chemical bonding frequently involves the application of the Schrödinger equation for the physical system in question and in so doing one does not pause to specify whether the bonding might be ionic or covalent. Give this state of affairs there would seem little point in attempting to specify the quintessential nature of just covalent bonding.

Further aspects of the Hendry's structural conception consist in the notion that ionic bonds are omnidirectional electrostatic interactions between positively and negatively charged ions while covalent bonds are regions of electron density that bind atoms together along particular trajectory.

The second sentence would seem to imply that ionic bonds do not involve regions of electron density, which is surely not what Hendry means to say. As to the question of directionality, this characterization would seem to omit an entire class of covalently bonded compounds such as diamond or graphite in which bonding is multi-directional just as in classic cases of ionic bonding.

Another philosopher of chemistry, Weisberg, drawing on Hendry, writes that,

Second, this [structural] conception says that bonding is a *sub-molecular* phenomenon, confined to regions between the atoms. This eliminates the possibility that bonds are a molecule-wide phenomenon (Weisberg, 2008, 935).

If this is intended as a further characteristic of just covalent bonding it is simply incorrect, since ionic bonding also occurs between atoms, or more correctly their ions. I am also puzzled by the apparent desire to exclude the possibility that bonds, or bonding, might be a molecule-wide phenomenon. Counter examples are easy to

⁷This point was already emphasized by G.N. Lewis almost exactly 100 years ago.

find. In addition to diamond and graphite, which are generally described as displaying giant covalent bonding, modern chemistry has revealed the frequent occurrence of delocalized bonding to occur in cases such as metals, conducting polymers, benzene and many other conjugated hydrocarbons. Moreover, delocalization of electrons is known to occur in many inorganic species such as oxyanions including the carbonate and sulfate ions. Bonding is indeed a molecule-wide phenomenon and delocalization is not confined to covalent compounds.

Thirdly, Robin Hendry⁸ believes that an article published by the late Gerome Berson provides support for own his view that bonds really exist between any particular two atoms in any molecule.⁹ In this article Berson reports on some unusual molecules which seem to support the notion that the energetic view of bonding is problematical. It should be emphasized that this conclusion was not in fact drawn by the author Berson but only by Hendry. The molecules in question are one labeled 9T which Berson compares with molecule 11 as shown in Fig. 8.1.

It appears that the more stable of the two molecules, 9T, possesses fewer bonds, as understood in the classical sense of the sharing of two electrons between any two given atoms. For Hendry this seems to indicate a violation of the equivalence between the extent of bonding and achieving the most stable energy. Molecule 9T appears to be more stable even though it has fewer bonds than molecule 11. Hendry's conclusion is that the energetic view provides an incomplete picture and that the structural view therefore appears to be superior in this instance.

I would like to propose looking at this issue from a different perspective. The fact that the molecule with fewer bonds is the more stable of the two, serves to illustrate that the naïve picture of 2 electrons to each bond between specific atoms might be where the problem lies. Far from supporting Hendry's position the molecule that

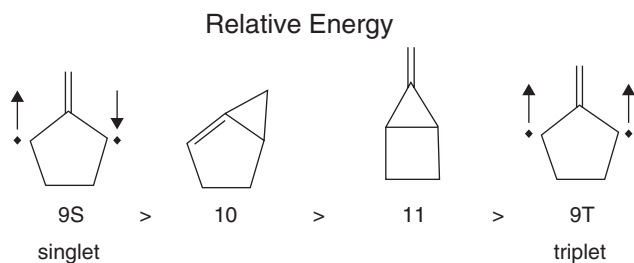


Fig. 8.1 Relative energies of singlet and triplet 2-methylenecyclopentane-1,3-diyl and their precursors (Berson, 2008, 951). (Reproduced with permission)

⁸Private E-mail correspondence with Robin Hendry.

⁹The article was based on a lecture given by Gerome Berson at the same session of the Philosophy of Science Association at which Hendry and Weisberg spoke in 2007. The only philosophical comment that Berson makes in his article is that, "Chemists therefore seek to enlist philosophers in sharpening the very definition of a bond." (p.947)

Berson has described, exposes the superficial nature of regarding bonds as specific inter-nuclear entities.

What this unusual molecule 9T shows, if anything, is that there appears to be a greater degree of ‘bonding’ despite the fact that there are fewer specific bonds in the naïve sense of the organic chemist. The degree of bonding in general thus remains correlated to the degree of energy minimization.¹⁰

Moreover, Berson’s analysis supports the view that the stability of molecules is the more important factor in considering the interconversion of molecules, regardless of precisely how many bonds are present in the classical sense of pairs of shared electrons. Or to cite Berson,

The bond concept allows us to understand much of chemistry, but far from all of it (Berson, 2008, 954).

Finally, I turn to an issue that represents perhaps the greatest threat to Robin Hendry’s view concerning the importance of the structural view, and his belief that bonds are ‘real’ in some unspecified way. In order to discuss this aspect, one must consider the quantum mechanical account of the covalent bond.

8.5 Quantum Mechanical Account of the Covalent Bond

Soon after Schrödinger published his wave equation for the hydrogen atom, two young post-doctoral fellows, Heitler and London, succeed in calculating the energy of the simplest molecule, H₂, and in showing that it was stable. In order to do so they drew on the fact that electrons acting through their wave nature would interact via constructive and destructive interference. The result of constructive interference is generally believed to be a build-up of electron density between the nuclei on adjacent hydrogen atoms, such that the two electrons that are shared in the covalent bond can be regarded as a form of ‘glue’ that causes the two positive nuclei to be attracted to each other. One apparent advantage of this interpretation is that it accords very well with the previous view of G.N. Lewis, namely that a covalent

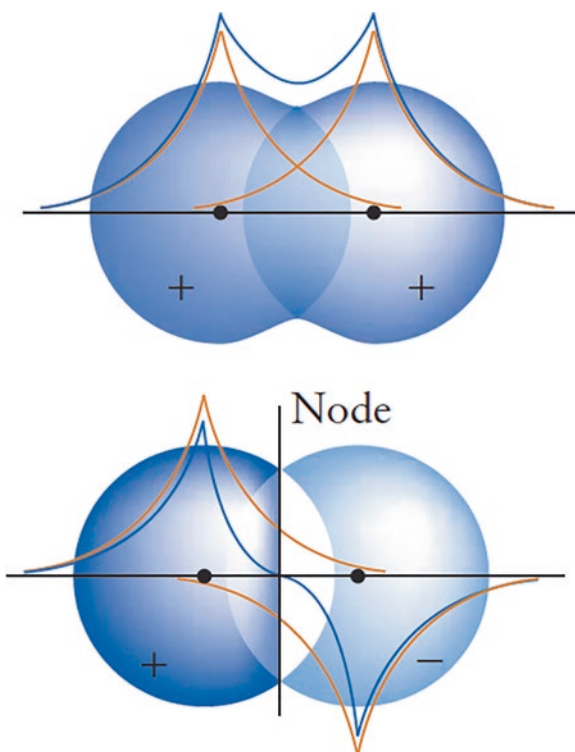
¹⁰In another figure, labeled 6, Berson connects structure 11 with structure 9S (a singlet species but having two unpaired electrons) over a transition state. Berson also connects 10 with 9S over another transition state. The author does not connect the 9T structure (a triplet species having two unpaired electrons) to any of the others because the triplet and singlets are of different symmetry and do not therefore couple or connect. It should also be noted that although structure 9T has fewer bonds than 11 or 10, (i) 9T has less internal strain energy within its ring than 11 (and maybe 10) and (ii) 9T is a triplet while the others are singlets. The importance of the latter statement can be appreciated by noting the 9S (which has fewer bonds just like 9T does) is actually higher in energy than 11 or 10. So, within the singlet world, the systems with more bonds (11 and 10) do indeed have lower energy than the system with fewer bonds (9S). The relative orderings of various structures depend on intrinsic bond strengths but also on strain energies as well as the energy difference between unpaired electrons in singlet or triplet couplings. I am grateful to Professor J. Simons for discussion on these issues.

Fig. 8.2 The conventional textbook explanation of bonding correctly begins by considering electron waves on adjacent atoms which combine together constructively and also destructively



The electron waves on each atom combine constructively as well as destructively.

Fig. 8.3 The top part of the image depicts constructive interference between waves on adjacent atoms leading to an increase in electron density between the nuclei. The lower part of the diagram depicts out-of-phase interaction leading to the depletion of electron density between the nuclei (Permission requested)

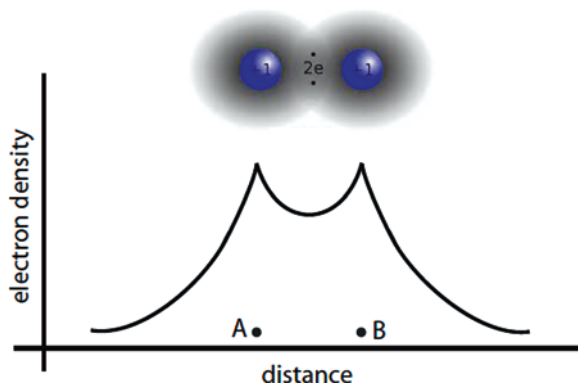


bond consists of a pair of electrons located mid-way between the two hydrogen atoms in the H_2 molecule.

The traditional interpretation of the quantum mechanical theory of chemical bonding arises from treating the electron as a wave and considering the interaction of the waves between two adjacent hydrogen atoms as shown in Fig. 8.2.

When any kind of waves combine together, they give rise to constructive as well as destructive interference. The former case results in a build-up of electrons between the nuclei. At the same time the destructive interference results in the depletion of electron density between the adjacent atoms as can be seen in Fig. 8.3.

Fig. 8.4 Constructive interference of electron waves as depicted in the upper part of Fig. 8.3 and the correspondence with the classical notion of a shared pair of electrons situated between adjacent atoms



The familiar textbook explanation of chemical bonding focuses primarily on the constructive interference contribution which serves to recover very much the same kind of picture of bonding as was first proposed by G.N. Lewis, namely that a covalent bond consists of a pair of electrons that are shared between adjacent atoms as illustrated in Fig. 8.4.

This conception of covalent bonding is somewhat erroneous since it ignores the contribution arising from destructive interference of the electron waves. Moreover, it is essentially an electrostatic view which ignores any contributions from the kinetic energy of the electrons. Whereas the calculations carried out by the likes of Heitler and London included kinetic energy terms in the Hamiltonian of the molecule, the simplified picture that we are discussing here would seem to be focusing exclusively on the potential energy contribution which is essentially static. The very notion of an electron glue situated in a particular location between the nuclei reinforces the notion of a static rather than dynamical view.

Fortunately, there is a long-standing line of argumentation among theoretical chemists that challenges this naïve notion. Beginning in the 1930s Hellman pioneered the view that covalent bonding was dominated by contribution of the kinetic energy of the electrons rather than their potential energy (Hellmann, 1937). For many years this view was ignored by most theoretical chemists until it was reformulated in a more rigorous fashion by the theoretical chemist Klaus Ruedenberg (Ruedenberg, 1962; Ruedenberg & Schmidt, 2007).

In order to illustrate the main ideas in the Hellman-Ruedenberg approach I now turn to an even simpler molecule than H_2 , namely the H_2^+ ion in which just a single electron is shared by the two adjacent hydrogen nuclei.¹¹ The Hamiltonian for this system is shown in Fig. 8.5.

In addition to calculating the total energy of the H_2^+ molecule-ion, it is possible to calculate the separate contributions due to kinetic and potential energy arising from the bonding and anti-bonding contributions due to constructive and destructive

¹¹The fact that this molecule-ion contains chemical bonding immediately belies the simple notion due to Lewis that a covalent bond consists of a *pair* of shared electrons.

The hydrogen molecule-ion

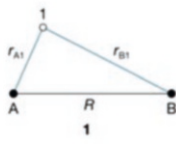
$$H = -\frac{\hbar}{2m_e} \nabla_1^2 + V \quad V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} + \frac{1}{R} \right)$$


Fig. 8.5 The Hamiltonian operator for the H_2^+ molecule-ion, in which V represents the potential energy which is made up of three terms

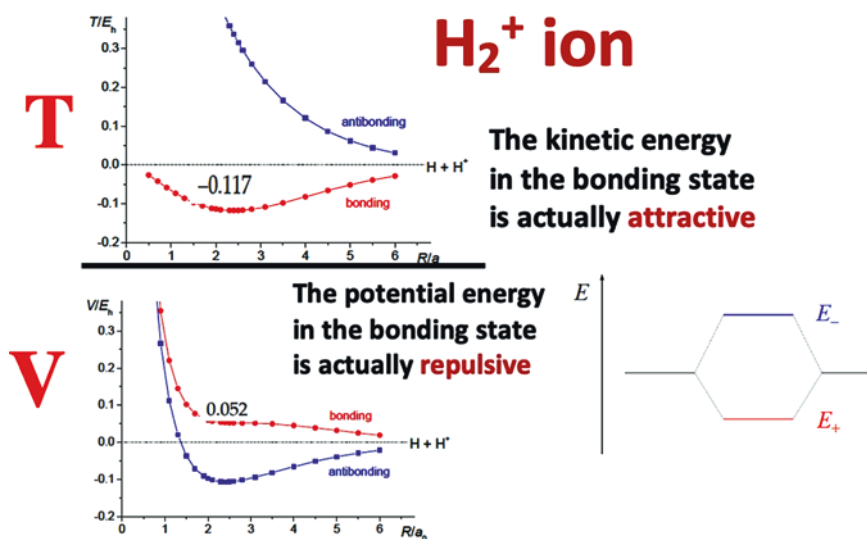


Fig. 8.6 Graphs of kinetic energy (T) and potential energy (V) as a function of internuclear separation. The attractive force is only present in the kinetic energy contribution to the total energy. (Diagram modified from Bacskay et al. (2010) and private correspondence with G. Bacskay)

interference respectively. The results of such calculations are displayed in Fig. 8.6 below. These graphs show very clearly that the attraction between the two hydrogen nuclei is due to the negative kinetic contribution and not to the contribution from the potential energy, which is in fact a positive and hence a repulsive term. The graphs also show that if the force responsible for bonding in this molecule-ion was due to potential energy alone, it would not lead to any bonding whatsoever, and there would be no means to overcome the repulsive force between the two positively charged hydrogen nuclei.

Given these facts it becomes difficult to maintain the classical view that a covalent bond consists of the sharing of electrons which are located between two adjacent atoms. More importantly for the main theme of the present article, it presents a major challenge for what Hendry has termed the structural view of chemical bonding which aims to recover directional bonds between particular atoms in a molecule and the notion that such bonds are somehow ‘real’. A more correct view according to the kinetic energy school of thought is to suppose that chemical bonding, rather than specific bonds, as such, is the result of electrons that are shared *by* nuclei but that do not necessarily lie between them. According to this view electrons are being shared by two or more atoms but not between these atoms.

Here is the way that one author expresses the alternative view of bonding,

The amount of electron density transferred to the bonding region is greatly overstated, sometimes implying that a pair of electrons is shared in the space between two nuclei rather than by two nuclei (Rioux, 2003).

8.6 Are Bonds Real?

A major pre-occupation for Hendry, among several philosophers of chemistry, has been the question of whether bonds are ‘real’ (Hendry, 2008; Weisberg, 2008; Seifert, 2022). For example, Hendry has attempted to refute the view of authors like Coulson who claimed that,

a bond ‘does not exist: no-one has ever seen it, no-one ever can. It is a figment of our own imagination (Coulson, 1955)

by appeal to Bader’s theory of atoms in molecules in which bond paths, rather than bonds, are a central feature of the theory. But as Hendry readily concedes, Bader’s view raises several conceptual problems, among them being the fact that it sometimes shows the presence of bond paths where they clearly cannot exist and in other instances represents a repulsive interaction as a bond path.

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 (Hendry, 2018, 113).

To conclude this section, I believe that the debate concerning the reality of bonds and the supposed opposition between the structural and energetic views are both vacuous. The alleged debate between the structural and the energetic view is essentially a return to the debate among chemists over the superiority of the valence bond or molecular orbital theories. Whereas bonds are regarded as real in the valence bond approach, molecular orbital theory assumes the presence of delocalized bonding but not specific bonds. The two approaches were shown to be completely

equivalent to each other by Slater and Van Vleck as early as the 1930s. Consequently there is no longer any debate over this question. Some philosophers of chemistry including Hendry and Weisberg are merely attempting to revive the same debate by asking the metaphysical question of whether bonds are 'real', but this does not alter the central issue.

As Paul Needham has written,

Construing the status of the chemical bond as an issue of existence, is perhaps an unfortunate formulation. What exists are entities such as molecules, atoms and electrons, whereas bonding is something they do. The question is How? (Needham, 2014, 11).

8.7 Conclusions

Hendry promotes the continuity of the concept of bonding. One may well agree with this notion of continuity in scientific concepts, as I have argued in a previous publication (Scerri, 2016). However, there is no denying that talk of bonds has now morphed into talk of 'bonding' in the quantum mechanical account. Bonding is now discussed in energetic grounds rather than via a realistic belief in entities that connect atoms together.

The notion that there are in fact two views of bonding is a relic of a debate that took place in the 1950s. The energetic view does indeed prevail over the structural view, if one must speak in these terms. Said otherwise, Slater and Van Vleck showed some 90 years ago that the valence bond and molecular orbital theories are completely equivalent mathematically (Slater, 1932; Van Vleck & Sherman, 1935).¹² Of course organic chemists may continue to regard bonds as pairs of electrons and may also think of molecular structure as being irreducible to quantum mechanics for the sake of expediency, but this does not sanction the ontological claim made by Hendry, to the effect that the structural and energetic views are still competing among each other as to which of them is the more correct description of chemical bonding.

References

- Bacskay, G. B., Eek, W., & Nordholm, S. (2010). Is covalent bonding a one-electron phenomenon? Analysis of a simple potential model of molecular structure. *The Chemical Educator*, 15, 42–54.
- Berson, G. (2008). Molecules with very weak bonds: The edge of covalency. *Philosophy of Science*, 75(5), 947–957.
- Coulson, C. A. (1955). The contributions of wave mechanics to chemistry. *Journal of the Chemical Society*, 2069–2084. <https://doi.org/10.1039/JR9550002069>

¹²Also see Galbraith et al. (2021) for a recent statement on the equivalence of the two theories and the manner in which they are frequently misrepresented in chemistry textbooks.

- Franklin, A., & Seifert, V. A. (2023). The problem of molecular structure just is the measurement problem. *British Journal for the Philosophy of Science*, 75. <https://doi.org/10.1086/715148>
- Galbraith, J. M., Shaik, S., Danovich, D., Braïda, B., Wei, W., Hiberty, P., Cooper, D. L., Karadakov, P. B., & Dunning, T. H., Jr. (2021). Valence bond and molecular orbital: Two powerful theories that nicely complement one another. *Journal of Chemical Education*, 98(12), 3617–3620.
- Gambini, R., & Pullin, J. (2020). *Loop quantum gravity for everyone*. World Scientific Press.
- Greenaway, F. (1966). *John Dalton and the Atom*. Cornell University Press.
- Hellmann, H. (1937). *Quantenchemie*. Deuticke, Leipzig and Wien.
- Hendry, R. (2008). Two concepts of chemical bond. *Philosophy of Science*, 75, 909–920.
- Hendry, R. F. (2010). Ontological reduction and molecular structure. *Studies in History and Philosophy of Modern Physics*, 41, 183–191. <https://doi.org/10.1016/j.shpsb.2010.03.005>
- Hendry, R. (2018). Scientific realism and the history of chemistry. *Spontaneous Generations: A Journal for the History and Philosophy of Science*, 9(1), 108–117.
- Jammer, M. (1966). *The conceptual development of quantum mechanics*. McGraw-Hill.
- Kossel, W. (1916). Molecule formation as a question of atomic structure. *Annalen der Physik*, 49, 229–362.
- Lange, M. (2013). What makes a scientific explanation distinctively mathematical? *British Journal for the Philosophy of Science*, 64, 485–511.
- Lewis, G. N. (1916). The atom and the molecule. *Journal of the American Chemical Society*, 38(1916), 762–786.
- Malrieu, J.-P., Guihéry, N., Jiménez Calzado, C., & Angeli, C. (2007). Bond electron pair: Its relevance and analysis from the quantum chemistry point of view. *Journal of Computational Chemistry*, 28, 35–50.
- Matta, C. (2023). Causal mapping: Some observations and questions by a chemist, A lecture delivered at the 2023 conference of Congress on Logic, Methodology and Philosophy of Science and Technology, Buenos Aires, Argentina (article in preparation).
- Mehra, J., & Rechenberg, H. (1987). *The historical development of quantum theory: Erwin Schrodinger and the rise of wave mechanics: The creation of wave mechanics early response and applications 1925–1926*. Springer.
- Needham, P. (2014). The source of chemical bonding. *Studies in History and Philosophy of Science*, 45, 1–13.
- Norton, J. D. (2003). Causation as folk science. *Philosophers' Imprint*, 3(4), 1–22.
- Primas, H. (1983). *Chemistry, quantum mechanics and reductionism perspectives in theoretical chemistry*. Springer.
- Rioux, F. (2003). The covalent bond examined using the virial theorem. *The Chemical Educator*, 8, 10–12.
- Rivadulla, A. (2019). Causal explanations: Are they possible in physics? Causal explanations: Are they possible in physics? In M. R. Matthews (Ed.), *Mario Bunge: A centenary festschrift*. Springer.
- Ruedenberg, K. (1962). The nature of the chemical bond. *Reviews of Modern Physics*, 34, 326.
- Ruedenberg, K., & Schmidt, M. W. (2007). Why does electron sharing lead to covalent bonding? A variational analysis. *Journal of Computational Chemistry*, 28, 391–410.
- Rzepa, H. (2009). The importance of being bonded. *Nature Chemistry*, 1, 510–512.
- Scerri, E. R. (2012). Top-down causation regarding the chemistry – Physics interface – A skeptical view. *Interface Focus*, Royal Society Publications, 2, 20–25.
- Scerri, E. R. (2016). *A tale of seven scientists and a new philosophy of science*. Oxford University Press.
- Scerri, E. R. (2020). *The periodic table, its story and its significance*. Oxford University Press.
- Scerri, E. R. (2021). Causation, electronic configurations and the periodic table. *Synthese*, 198, 9709–9720.
- Seifert, V. (2022). The chemical bond is a real pattern. *Philosophy of Science*, 1–47. <https://doi.org/10.1017/psa.2022.17>. Published online, 22nd April.
- Slater, J. C. (1932). Note on molecular structure. *Physics Review*, 41, 255–257.

- Van Vleck, J. H., & Sherman, A. (1935). The quantum theory of valence. *Reviews of Modern Physics*, 7, 167–228.
- Weisberg, M. (2008). Challenges to the structural conception of chemical bonding. *Philosophy in Science*, 75, 932–946.
- Woolley, G. (1976). Quantum theory and molecular structure. *Advances in Physics*, 25, 27–52.
- Zurek, W. H. (2003). Decoherence, einselection, and the quantum origins of the classical. *Reviews of Modern Physics*, 75, 715–775.

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