The Development of the Idea of a Chemical Bond

BRIAN T. SUTCLIFFE

Department of Chemistry, University of York, York YO1 5DD, United Kingdom

ABSTRACT

The development of the idea of a chemical bond is traced from Frankland to Heitler and London and beyond with emphasis on how electrons came to be considered essential to explaining the bond. © 1996 John Wiley & Sons, Inc.

Introduction

Most historians of chemistry now agree that Frankland was responsible for inventing the chemical bond. According to Russell [1], the first formal statement of the idea of a bond appeared in Frankland's article in *J. Chem Soc.* **19**, 377 (1866). In that article, Frankland said:

> By the term *bond,* I intend merely to give a more concrete expression to what has received various names from different chemists, such as an atomicity, an atomic power, and an equivalence. A monad is represented as an element having one bond, a dyad as an element having two bonds, etc. It is scarcely necessary to remark by this term I do not intend to convey the idea of any material connection between the elements of a compound, the bonds actually holding the atoms of a chemical compound being, as regards

their nature much more like those which connect the members of our solar system.

The idea of representing a bond by means of a straight line joining the atomic symbols we probably owe to Alexander Crum Brown. (He was very long-lived, from 1832 until 1922, and as a young man, the author met someone who had actually been taught by him at the University of Edinburgh.) Frankland, with due acknowledgment, adopted Crum Brown's representation (which put circles round the atom symbols), but by 1867, the circles had been dropped and more or less modern chemical notation became widespread. This was, in some measure, almost certainly because of the ease with which isomers of hydrocarbons could be represented and enumerated within this approach, as shown especially in the work of Cayley [2].

What is notable here is Frankland's extreme caution "to avoid any speculation as to the nature of the tie which enables an element thus to attach itself to one or more atoms of other elements" [1]. The historical reasons for this caution are not hard to fathom, but what is rather harder to understand

is why, within 40 years of it being made, chemists (with some notable exceptions) were happy to throw caution to the winds and espouse the electron as the originator of the chemical bond. In this article, I consider how this came about and to what it led after the advent of modern quantum mechanics.

In describing what went on, I rely chiefly on secondary sources and it is in these that the references to the primary material may be located. Among the secondary sources consulted were Russell [1], Lagowski [3], and Stranges [4]. Brock, in his *History of Chemistry* [5], devoted a chapter to the bond in the context of a general history (published in the U.S. by Norton and in Europe by Fontana). A work which provides a context within which the development of the idea can be seen in a most helpful way is the book *From Chemical Philosophy to Theoretical Chemistry* by Nye [6].

The Bond and the Electron Until the Beginning of the Twentieth Century

The idea of a chemical combination as being due to electrical forces has, of course, a long history in chemistry. It is probably not unfair to attribute to Berzelius the early development of the important ideas here, but the rise of organic chemistry, in which the combination was not obviously of an electrical kind, led to the eclipse of his approach. The theory of types and the theory of radicals both bid to replace it. It was not until the 1850's that the idea of atoms having autonomous valencies developed, and through this idea (which he played an important part in developing; see, e.g., [1, 3], Frankland arrived at the idea of a chemical bond. His caution about saying precisely what a bond was was probably due to his desire not to give hostages to fortune in a way that could give support to those adherents of either of the older theories of chemical combination. It could also have had something to do with the philosophical controversies about the real existence of unobservable entities, such as atoms and molecules, which was then a lively part of the discussions current in scientific and learned circles. It is interesting to remember that the distinguished Anglo–American mathematician Sylvester wrote an article in 1878 [7] whose aim was to show how graphical formulas for molecules could be realized in purely algebraic terms. (Sylvester called his

algebra "the algebra of binary quantics," but we should today call it the theory of binary or bilinear forms.) The reasons that he chose to do this can, at least in part, be inferred from the following quotations:

> Chemical graphs, at all events, for the present are to be regarded as translations into geometrical forms of trains of priorities and sequences having their proper *habitat* in the sphere of order and existing quite outside the world of space. Were it otherwise, we might indulge in some speculation as to the directions of the lines of emission or influence or radiation or whatever else the bonds might then be supposed to represent as dependent on the manner of the atoms entering into combination to form chemical substances. Such not being the case....

The perhaps unworthy suspicion does enter one's mind that Sylvester founded and was first editor-in-chief of the *American Journal of Mathematics*, in which his article appeared, to get things like this off his chest. This suspicion is supported somewhat by the following, in which some rather sententious thoughts are expressed:

> In regard of atomicity theory (*read* "valency theory"), all these modes of colligation are identical, and the supposition that there is any real difference between them, or that figures in space are distinguishable from figures in a plane (as I heard suggested might be the case by a high authority at a meeting of the British Association for the Advancement of Science, where I happened to be present), is a departure from the cautious philosophical views embodied in the theory as it came from the hands of its illustrious authors and continued to be maintained by their sober-minded successors and coadjutors, and affords an instructive instance of the tendency of the human mind to worship, as if of self-subsistent realities, of the symbols of its own creation.

The idea of directed valence was, of course, 4 or so years old by the time Sylvester wrote this and he was not the only one who opposed van't Hoff and le Bel. Kolbe (with whom Frankland actually published an article on valence in 1857), in particular, remained vociferous in his opposition to the idea until his death in 1884. (An account of Kolbe's

extreme reaction to the article of van't Hoff on the tetrahedrally directed bonds in carbon can be found in the entertaining book by Klotz [8] and Kolbe's position is examined, in context, in Russell's book.) There was also an extremely radical suggestion made in 1866 by Sir Benjamin Brodie [9], Waynflete professor of chemistry in the University of Oxford, that not only bonds should be treated as imaginative constructions but that so also should atoms. His *Calculus of Chemical Operations*, he asserted, was based on no theories about anything but simply on observations. Again, some feeling for how these ideas were received can be gained from Russell's book and also from an article by Farrar [10]. (It is clear from his article that Farrar regards Brodie as just about fit for the funny farm, which I think rather unfair, but it is difficult to regard him as other than pretty eccentric by the time of his second article in 1877 [11].)

In his article, Sylvester actually first attributed the idea of a bond to Kekulé and corrected himself only in a footnote toward the end of the first appendix. Frankland, however, clearly kept an eye open for his priority and wrote a letter to Sylvester, which Sylvester published, just to keep things straight. At the end of this letter [12], Frankland said:

> I trust that you will go on with the consideration of chemical phenomena from a mathematical point of view, for I am convinced that the future progress of chemistry, as an extact science, depends very much indeed upon the alliance of mathematics ....

I cannot make up my mind as to whether or not Frankland had his tongue in his cheek when he wrote that. If he had really felt that, I feel that he would perhaps of been more supportive of Sir Benjamin Brodie during the atomic debates that followed Brodie's first article (see [13]). But perhaps Frankland's pragmatic attitude prevented this. Sylvester, too, must have known of Brodie's work (he had an article that appeared immediately before Brodie's first article in *Philos. Trans.*) but he never mentions him at all. As far as chemists were concerned, Brodie was undoubtedly an embarrassment and they do not seem to have thought much of Sylvester's ideas either. But it is interesting to note that Sylvester's approach did seem to influence Matsen [14] in the 20th century, in the development of his spin-free quantum chemistry.

The graphical notation and the ideas of Frankland were further developed by Werner in the 1890s in his coordination theory for inorganic complexes, but it was during this period that the first tentative steps were made toward an electronic theory of the chemical bond following J. J. Thomson's discovery of the electron in 1897.

Atomic structure seems first to have been related to valency when both Mendeleef and Lothar Meyer had observed, independently, in the late 1860s how valency was correlated with position in the periodic table. It was also, perhaps in the air, for in his 1881 Faraday lecture that Helmholtz revived and expanded the electrical theory of chemical combination. The connection between the electron and bonding originates with Thomson's association of the electron with the structure of the atom. By 1902, Oliver Lodge in his Romanes Lecture discussion of chemical union could say (as quoted in Stranges [4]) that:

> It becomes a reasonable hypothesis to surmise that the whole of the atom may be built up of positive and negative electrons interleaved together, and of nothing else; an active or charged ion having one negative electron in excess or defect, but the neutral atom having an exact number of pairs.

He then goes on to say that chemical combination must be the result of the pairing of oppositely charged ions. Lodge was, of course, developing the ideas of J. J. Thomson in the context of Helmhotz's ideas. At this time, no positive electrons had been observed and, after Rutherford's construction of the nuclear atom in 1911, the positive electron became irrelevant in discussions of bonding.

Ideas very similar to those of Lodge were forming in the mind of G. N. Lewis at about this time (1902) but they were not published until 1916, after the Bohr atom ideas had become prominent in physics.

It is difficult to avoid presenting too "triumphalist" a view of the history of the development of the idea of a bond from now on. How things actually developed is now known and seems as if it were foreordained. The history of the period after the discovery of the electron and up to the coming of wave mechanics is surveyed in some detail in the book by Stranges and in outline in the book by Russell and in the book by Lagowski [3]. But since it was Lewis's ideas that were influential, it is on Lewis that I shall concentrate. It was

Lewis' skillful combination of electronic ideas with traditional ideas of the bond that proved so persuasive to chemists.

The Bond from Lewis to Pauling

In his 1923 book, Lewis [15] said the following about the development of his theory:

> In the year 1902 . . . , I formed an idea of the inner structure of the atom which, although it contained certain crudities, I have ever since regarded as representing essentially the arrangement of electrons in the atom . . . .
>
> The main features of this theory of atomic structure are as follows:
>
> 1. The electrons in an atom are arranged in concentric cubes.
> 2. A neutral atom of each element contains one more electron than a neutral atom of the element next preceding.
> 3. The cube of eight electrons is reached in the atoms of the rare gases, and this cube becomes in some sense the kernel about which the larger cube of electrons of the next period is built.
> 4. The electrons of an outer incomplete cube may be given to another atom, as in Mg^{++}, or enough electrons may be taken from other atoms to complete the cube, as in Cl^-, thus accounting for "positive and negative valence."

Although it is proper to accord Lewis the intellectual priority here, the priority in publication of the "octet rule" is actually by Abegg in 1904 [16]. Lewis did not publish until 1916 [17], and he was nearly pipped at the post by Kossel [18], who had arrived at very similar conclusions by this time. However, in his article, Lewis introduced a new idea and a new means of representation, and these new things are quite unambiguously Lewis' contributions alone. The new idea was the "rule of two" in which he asserted that the occurrence of electrons in molecules in even numbers was pretty much universal. The new means of representation was the method of symbolizing electrons by dots, which is now so familiar to us. The ability to make the correspondence of a pair of dots between two atom symbols and the bond in this representation made it extremely attractive to working chemists. Lewis' approach carried the day and this was in no small measure due to the effectiveness of Langmuir as his fugleman (though this relationship was not without its strains as evidenced in Stranges' book).

The interesting things to notice, I think, are that the ideas here owe absolutely nothing to quantum mechanics and certainly nothing to Bohr, and, also, that the model of the atom that is presupposed is a static one. It would be wrong to believe that this was because those involved in the developments here did not know what was going on in physics. They knew very well and were, on the whole, pretty sceptical about them. At a meeting of the AAAS in New York in December 1916, Lewis devoted his address to the idea of a static atom [19], and he actually said:

> Unless we are willing, under the onslaught of quantum theories, to throw over all the basic principles of physical science, we must conclude that the electron in the Bohr atom not only ceases to obey Coulomb's law, but exerts no influence whatsoever upon another charged particle at any distance.

This absence of the effect, Lewis considered logically and scientifically objectionable, for, he said [17]: "that state of motion which produces no physical effect whatsoever may better be called a state of rest."

And he was not alone in his scepticism. J. J. Thomson was trying to work a static atom theory as late as 1923 as were Langmuir, Davey, Born, Landé, and Parson. All involved were trying to modify Coulomb's force law to get a theory in which the electrons in an atom remained still and were distributed at the corners of a cube. But in his Nobel lecture in 1922, Bohr delivered an attack on static atom theories, pointing out that Earnshaw's theorem showed that a static distribution of charges must be unstable if Coulomb's law applies and extending the argument to cover the proposed modified potentials.

This clearly was, at least, a very uncomfortable situation for chemists and some undoubtedly thought it intolerable. Among those who did was Sidgwick who attempted to avoid the difficulty by shifting the argument away from atomic structure as such, to the idea of molecular structure in which pairs of electrons had common orbits of the Bohr–Sommerfeld type involving the molecular

nuclei. He seems to be the first person to point out that it was possible to imagine a dynamical situation in which a pair of electrons could hold a pair of nuclei together. This suggestion was made at a meeting of the Faraday Society in Cambridge in 1923 [20], and at that meeting, Lewis in his introductory address signaled his accession to a similar point of view and his mature views are expounded in his book [15] as those of Sidgwick are in his 1927 book [21]. Lewis is clearly still unhappy with quantum theory, for in the closing pages of his book, he cannot resist referring to it as "the entering wedge of scientific bolshevism," but Sidgwick had decided to bite the bullet. The preface to his book begins:

This book aims at giving a general account of the principles of valency and molecular constitution founded on the Rutherford–Bohr atom.
In developing the theory of valency there are two courses open to the chemist. He may use symbols with no definite physical connotation ... or he may adopt the concepts of atomic physics, ... and try to explain chemical facts in terms of these. But if he takes the latter course, as is done in this book, he must accept the physical conclusions in full ....

But, then, it is clear that he sensed the "cloud no bigger than a man's hand" on the horizon when he acknowledged the newly published work of Schrödinger and said:

It has yet given no proof that the physical concepts which led (him) to his fundamental differential equation should be taken so literally as to be incompatible with the conceptions of the nature of electrons and nuclei to which the work of the last thirty years has led.

In fact, Sidgwick's book was a threnody for the old way of looking at things, for Heitler and London's article appeared in that year and it fell to Pauling to make what reconciliation was possible between the Lewis theory and the approach made by Heitler and London. This he did in a series of articles published between 1928 and 1933 and whose conclusions are brought together in his book [22], dedicated to G. N. Lewis and published in 1939. In this enormously influential book, Pauling

had a clear program. He said:

I formed the opinion that, even though much of the recent progress in structural chemistry has been due to quantum mechanics, it should be possible to describe the new developments in a thorough-going and satisfactory manner without the use of advanced mathematics. A small part only of the body of contributions of quantum mechanics to chemistry has been purely quantum mechanical in character.... The advances which have been made have been in the main the result of essentially chemical arguments.... The principal contribution of quantum mechanics to chemistry has been the suggestion of new ideas, such as resonance....

Pauling starts his exposition from the idea of the electron pair bond as envisaged by Lewis and shows how this can be understood in the context of the Heitler–London calculation as being due to strong orbital overlap. After introducing the idea of orbital hybridization, he then uses the idea of maximum overlap in discussing bonding generally. It is an amazing *tour de force* with just enough mathematics to provide "corroborative detail, intended to give artistic verisimilitude to an otherwise bald and unconvincing narrative" (to misappropriate Pooh-Bah's lines from *The Mikado*) and not too much to be daunting. I feel sure that every practicing latter-day quantum chemist must envy Pauling his facility and wish that they had written the book. (Though perhaps some might have wished, on similar grounds, to have written Coulson's *Valence*.) It brought quantum mechanical ideas into chemistry in an unthreatening way by realizing the electron pair bond in terms of hybrid orbitals, maximally overlapping. It dealt with the problems that arose when equivalent pairings were possible, by a judicious use of resonance. Thus, once the book's ideas had been assimilated, chemists could carry on in much the same way as had been the case formerly but with resonance and hybrids added to their armory. And they did so with the comforting feeling that the most sophisticated theory in modern mathematical physics supported their actions.

It should not be thought, however, that all were convinced as was Pauling in the correspondence between perfect pairing and the bond. Mulliken arrived at very different conclusions from the standpoint of molecular orbital theory. He devoted

his 1931 review [23] to a description of molecular structure in terms of molecular orbitals, and at the end of the last section, felt constrained to say:

> The fact that valence electrons almost always occur in pairs in saturated molecules appears to have after all no fundamental connection with the existence of chemical binding. . . .
>
> A clearer understanding of molecular structure . . . can often be obtained by dropping all together the idea of atoms or ions held together by valence forces, and adopting the molecular point of view, which regards each molecule as a distinct individual built up of nuclei and electrons.

For Mulliken at least, it was clearly somewhat doubtful even then that the bond was either necessary for or explicable in terms of the quantum mechanics required to account for molecular structure.

A very interesting and balanced account of the field at about this time can be found in the 1935 review "The Quantum Theory of Valence" by Van Vleck and Sherman [24]. On the whole, the review seems to regard the molecular orbital viewpoint as being the more satisfactory one and maintains Mulliken's scepticism about the importance of electron pairs.

The Bond from Pauling to the Supercomputer

In all the schemes proposed at this time for doing molecular calculations, the nuclei were treated as providing a molecular geometry, in terms of which a molecular electronic structure calculation was parameterized, i.e., the nuclei were considered as essentially classical particles, which could be clamped at will to construct a molecule with a chosen geometry. This was the approach used by Heitler and London in their pioneering calculation and it became usual to say that it was justified "within the Born–Oppenheimer approximation."

The fascinating thing about the actual computational developments in this period, however, was that almost none used the approach, the so-called valence bond (VB) approach, that Pauling had proposed as the foundation of the theory of the bond.

The technical reasons for this are well enough known. The nonorthogonality between the hybrid orbitals, a feature essential for the justification of the Pauling approach, made formulating the equations for calculation just too complicated and difficult, and even if approximations were made, but made in a consistent fashion, any consequent calculations were impossible to perform. It was thus not possible to provide a means of tying Pauling's ideas to the detailed equations in any unambiguous way.

In fact, almost all went the way that Mulliken proposed using a molecular orbital approach. In this approach, it was possible to formulate the equations in a manner suitable for calculation and to develop consistent approximation schemes that allowed at least semiempirical calculations to be made. A number of semiempirical schemes were developed, particularly for aromatic and conjugated systems, which can be regarded as inspired by the initial efforts of Hückel in 1931 to use molecular orbitals in this area. For such systems, the idea of a delocalized electron distribution came immediately out of the calculations, so that there was no need to invoke the bond or the idea of resonance. However, the parameterization schemes within these semiempirical approaches were cast in terms of integrals between hybrid orbitals, so that aspect of Pauling's ideas remained alive both in chemistry and in quantum chemistry.

The principal computational approaches to molecular electronic structure that developed from about 1950 onward had molecular orbitals (MOs) as their basis. Since the MOs were realized in terms of linear combinations of atomic orbitals (LCAOs), the orbital remained a feature of the quantum mechanical account of molecular structure. Initially at least, it was not possible to realize fully the LCAO MO approach because, except in diatomic systems, the integrals over the orbitals, which were exponential in their radial parts (Slater orbitals), proved too difficult to evaluate quickly enough to make nonempirical calculation feasible. But even given these limitations, it was already clear that the role of the bond in the emerging discipline of computational quantum chemistry was going to be problematic.

The state of affairs at this stage was well summed up by Coulson in his 1951 Tilden Lecture [25], "The Contributions of Wave Mechanics to Chemistry." In his lecture, he dwelt on three topics: the simple chemical bond, π-electron chemistry, and chemical reactivity and it is the first of

those topics that is of interest here. Coulson used the idea of hybrid orbitals in discussing bonds and molecular shape, as might have been expected, but the ground is shifting a little. He takes the electronic charge density as the origin of binding:

> We might say that the description of a bond is essentially the description of the pattern of the charge cloud.... Indeed in the very last resort, we cannot entirely separate the charge cloud for one bond from that for another bond. But, subject to reasonable limitations...they can be found in terms of suitable patterns...for the isolated atoms.

And, of course, this position presages much work done on in attempts to picture the bond as related to the electronic charge density between the nuclei. The first quantitative attempt here is probably by Berlin [26], who in 1951 tried to use the Hellmann–Feynman theorem to account for the bond in terms of electrostatic forces engendered by the charge cloud. The bond analysis of charge densities has been extensively developed by Bader and his co-workers; see, e.g., [27]. This viewpoint has encouraged some experimental work to try to "see" the bond by looking for localized charge densities in molecules and some of this work was reviewed in [28].

Yet, in the closing section of his lecture, Coulson seemed not quite sure that he was on the right track. In fact, he adopted a really rather positivistic attitude, reminiscent if not of Brodie then perhaps of Sylvester at least. He said:

> I described a bond, a normal chemical bond; and I gave many details of its character (and could have given many more). Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. And then I awake with a little shock: for a chemical bond is not a real thing: it does not exist: no-one has ever seen it, no-one ever can. It is a figment of our own imagination.

A certain scepticism, perhaps not quite as marked as in the quote above, also found its place in Coulson's after-dinner speech entitled "The Present State of Molecular Structure Calculations" [29], made at the Boulder Conference in 1959. He said there:

> The concepts of classical chemistry were never completely precise.... Thus when we carry these concepts over into quantum chemistry we must be prepared to discover just the same mathematical unsatisfactoryness [sic].

In the nearly 10 years since Coulson's Tilden Lecture, enormous developments had been made in electronic computers and schemes for the calculation of molecular electronic structure were already far advanced, though not to be completely realized for another 10 years, with the further developments in integral schemes. It was against this background that Coulson introduced the celebrated idea of the two groups of quantum chemists. Group I were those who wanted to do as accurate calculations as possible and who believed that the role of wave mechanics was to obtain numbers. Group II were those who believed that its role was to account for the "quite elementary" concepts of ordinary chemistry. For those in group I, Coulson maintained:

> Mathematically..., a bond is an impossible concept.... It is not surprising...therefore that it is practically never used by them. Yet the existence of bond properties is basic to all chemistry.

In these circumstances, it is perhaps not surprising that Coulson was pessimistic about whether for much longer the two groups would continue to speak to one another. He opined that "there is now little point in bringing them together. This is probably the last conference of the old kind."

But with his customary perspicuity, Coulson had touched the nerve of the problem and what he said about computational quantum chemists and the bond needs no modification even to this day. Those who compute structure can often find ways of getting bonds and the like out of their results. In constructing trial wave functions, they are often guided by classical chemical structure considerations. But it is perhaps not too much to say that in these contexts the perceived role of the bond is that either of decorative embellishment in the first instance or of intellectual scaffolding in the second. For the computational quantum chemist, the legitimacy of a molecular structure is decided by the calculation. Though such a person appreciates the

aid of scaffolding and the appeal of decoration, both, in the last analysis, can be done without.

One of the ways in which a wave function can be analyzed in a manner suggestive of a particular pattern of bonds is if important elements of the wave function can be seen as consisting of strongly overlapping orbitals. It is in this context that there has been much discussion in the chemical education literature over the past 10 or so years about what should be taught about the bond in the light of present knowledge. The sequence of articles, between which and from which there are many cross references, begins with some fairly radical thoughts by Bent in two articles [30, 31] on atoms. But things began to warm up in an article by Ogilivie entitled, "There Are No Such Things As Orbitals" [32] in 1990. This generated a flurry of responses [33–37] and, eventually, a thunderous response from Pauling [38]. Pauling clearly felt that he had dealt effectively with the whole controversy, for he ends a magisterial last section, entitled "The Consequent Implications for Chemical Education," with the observation that the information that has recently become available

has not decreased the value of the concept of the chemical bond. I am pleased and gratified that in 1992 the chemical bond is alive and well.

All these articles appeared in *The Journal of Chemical Education*, and in the fashion of editors everywhere in exchanges of this kind, the editor declined to print any more contributions to the debate after Pauling's response. However, Ogilivie provided a summary of and a commentary on the whole exchange in his article [39]. The commentary does not pretend to be impartial.

As noted earlier, all the discussion so far has been in the clamped nucleus approximation for electronic structure calculations. The wave function of interest, in terms of which all the above discussion has taken place, is the electronic wave function for the molecule at its equilibrium nuclear geometry. The equilibrium geometry is supposed to be that nuclear geometry which minimizes the sum of the electronic energy and the nuclear repulsion energy, this last calculated classically. As a matter of fact, this process actually breaks the permutational symmetry of the quantum mechanical problem by identifying the nuclei. This seems first to have been mentioned in print by Berry in 1960 [40], and this early article attempted to deal

with what Weininger so perceptively recognized, somewhat later, as much more radical objections to the idea of molecular structure and bonds [41]. These are about whether you could actually get the bond and molecular structure out of quantum mechanics without making assumptions about the way the nuclei moved.

Deconstructing the Bond

For many involved in thinking about the problem of molecular structure, and, hence, of the chemical bond at this level, it seems as if it is the old philosophical problem of reductionism that is at the center of their anxieties. In general, it is those quantum chemists who discount the value of a reductionist perspective, who tend to be most sceptical about the possibility of accounting for molecular structure in terms of quantum mechanics. It is odd, too, that their opponents in argument, generally, are also opposed to reductionism, in the sense that they would certainly resist attempts to account for chemistry as a branch of physics or even to account for organic chemistry as a branch of physical chemistry.

Perhaps the widest-ranging account of the problem of molecular structure is in the book by Primas [42]. This book is very radical in its attempts to undercut *any* reduction through quantum mechanics to chemical ideas. In the precise area of bonding and molecular structure, the important radical work is that of Woolley [43–51] and that of Claverie [52, 53].

In general terms, the arguments are that if one knew only the isolated molecule Schrödinger equation and knew nothing of classical molecular structure theory then there is nothing that would lead one to expect molecule-like solutions among its eigenstates. Indeed, there is actually much that would make one hesitant about even *looking* for such solutions. Thus, as Woolley pointed out, a natural element of classical molecular structure theory is to assign static dipoles to particular molecules. Such assignments are often made in terms of vector sums of bond dipole moments, so that bonds are deemed to play an important role in static molecular dipoles. But the Schrödinger Hamiltonian commutes with the inversion operator, so its eigenstates must be parity eigenstates and, hence, must have zero expectation values for the static dipole operator. But if an eigenstate

corresponds to a molecule with structure, then, it follows, that the molecule cannot have a static dipole moment. The result cannot be doubted, but it has a very paradoxical flavor. A similar argument, as again Woolley showed, leads to the conclusion that the existence of stereoisomers cannot be accounted for in terms of solutions of the Schrödinger equation. Similarly, it is perfectly well known that an electric dipole transition in a rotating–vibrating molecule cannot occur without a change in the principal rotational quantum number J. The argument here is again one based entirely on symmetry and the invariances of the Schrödinger Hamiltonian. Thus, on the face of it, a pure vibrational spectrum is not explicable in terms of Schrödinger wave functions.

Woolley also made the point most eloquently in his discussion of the isomers of polyatomic molecules, [48, 51] that what one might think of, e.g., as the molecular Hamiltonian for cubane, C_8H_8, is also the molecular Hamiltonian for cyclooctatetrene, vinylbenzene, and many other systems, too. Indeed, it is even the Hamiltonian for a system with optical isomers, 3-vinyl hexa-1,4-diyne, which has the molecular formula

$$CH_2{=}CH{-}\overset{\displaystyle H}{\underset{\displaystyle C{\equiv}C{-}CH_3}{C}}{-}C{\equiv}CH$$
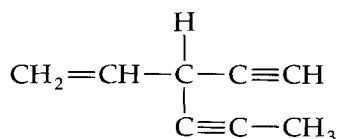
and in which the central carbon is clearly chiral by the conventional rules.

Thus, the idea of a molecule with a particular structure is, at best, only implicit in any molecular Hamiltonian and criteria other than purely quantum mechanical ones are therefore *logically* necessary to identify a particular solution as the chemical molecule. A similar point can be made in terms of chemical reaction schemes, for there the Hamiltonian for the products must be identical with the Hamiltonian for the reactants.

Examples of these apparently paradoxical results could easily be multiplied and, for some radical thinkers, indicate that the Schrödinger equation for the isolated molecule cannot be the appropriate equation with which to describe molecular structure. Thus, it is sometimes maintained that molecular structure appears only when the molecule is considered as surrounded by other molecules or in its interaction with the vacuum field and so on. Certainly, these ideas are in tune with more modern thinking about the holistic

nature of quantum mechanics that has developed since the work of Bell on the Einstein–Podolsky–Rosen paradox. (For a cheerful account of the work of Bell, see the articles collected in the book by Mermin [54].)

However, it is actually possible to rescue particular aspects of molecular structure even from full solutions to the equation by adopting tactics much like those used in getting bonds out of clamped nucleus calculations. For example, it is perfectly easy to show that given certain detailed assumptions about the form of the wave function that describes the molecule undergoing the dipole transition spoken of above then the idea of a pure vibrational transition can be rescued from mathematics. The assumptions that have to be made are essentially those made by Eckart in designing his body-mixed frame [55], which enables the wave function to be written as a product of a vibrational part with an independent rotational part. A detailed study of this with some numerical results for triatomic systems can be found in le Sueur et al. [56]. Of course, such approximations will not always work but it is arguable that they fail just where it is unreasonable to persist with the classical idea of molecular structure. Rather general discussions of what might be involved in constructing and processing solutions of the Schrödinger equation with a view to extracting molecular structure from them can be found in two articles by Sutcliffe [57, 58]. There are also articles on models of chemical bonding in the collection edited by Maksić [59].

It is thus arguable that if you know what you want to get out of the full wave function then you can usually get it by the use of suitable approximations. In this view, the position in the full wave function case is not too different from that described earlier when talking about results obtained in the fixed nucleus approximation. The idea of molecular structure and the consequent idea of a bond can then be accounted for in an approximate and not entirely coherent way whenever it seems important to do so. However, accounting for molecular structure, and, hence, the bond, in terms of straightforward recognition in the wave function is still an open problem here. In this view, if you want it out, you have to put it in.

Naturally, this position cannot be taken without some feelings of anxiety, for it is perfectly conceivable that the explanation that is offered of chemical behavior in terms of molecular structure and bonding could be somehow misleading. It could,

perhaps, prevent us seeing more deeply into the nature of things. If we were to clear our minds of our classical preconceptions and pay more attention to the quantum mechanics, then we might see more.

Conclusions

There are, of course, no firm conclusions to be offered on a topic like this at this stage of its development and it is perhaps hazardous even to offer an opinion. But I think that most chemists would agree that any theory is a work of the imagination. They would thus agree with Coulson in recognizing the bond as a figment of our imagination. However, I think that few would seriously doubt the utility of the idea of a bond in the standard explicatory scheme. Few would say that there is no such thing as a chemical bond. Most would agree that the bond has a perfectly satisfactory existence as a logical construct in a highly developed and extremely effective theory of molecular structure. However, I am sure that many, if not most, quantum chemists performing calculations in the clamped nucleus approach would agree that the role that it plays in that theory cannot be reduced in any invariant way to an aspect of quantum mechanics. So, it is at least arguable that, from the point of view of quantum chemistry as usually practized, the supercomputer has dissolved the bond.

In the context of solutions to the full Schrödinger problem, personal inclination is to agree with Charles Coulson's Tilden Lecture position even here and to think that, subject to reasonable limitations, molecular structure can still be found if you know what you are looking for. I acknowledge that the radicals could be right but, again with Coulson, I think that it is worthwhile to adopt pragmatic schemes for getting molecular structure out of wave functions whenever possible. I think that such pictures seldom mislead seriously whenever it is possible to draw them. However, I think that it will be unrewarding to search for a perfectly mathematically satisfactory invariant way of accounting for the bond by analyzing a wave function.

If I were to guess the future, I should guess that the idea of the bond and of molecular structure will prove rather slippery when it comes to interpreting the results of really high-precision spectro-scopic experiments. I think that it will also prove unhelpful in the study of highly excited states. But in most other areas, particularly organic chemistry and biochemistry, I feel that I should have to follow Pauling and predict, that there, the bond will remain alive and well.

This article is offered to Jens-Peder Dahl on the occasion of his 60th birthday. It is offered in grateful acknowledgement of my trust in the thoughtfulness and honesty of his opinions in all intellectual matters and the consequent confidence that I have always placed in them. It is offered, too, with thanks for friendship over many years. *Rara temporum felicitas ... quae sentias dicere licet.*

References

1. C. A. Russell, *The History of Valency* (Leicester University Press, Leicester, 1971).
2. A. Cayley, *Philos. Mag.* **67**, 444 (1874).
3. J. J. Lagowski, *The Chemical Bond* (Houghton Mifflin, Boston, 1966).
4. A. N. Stranges, *Electrons and Valence* (Texas A & M University Press, College Station, 1982).
5. W. H. Brock, *The Fontana History of Chemistry* (Fontana, London, 1992).
6. M. J. Nye, *From Chemical Philosphy to Theoretical Chemistry* (University of California Press, Berkeley, 1993).
7. J. J. Sylvester, *Am. J. Math.* **1**, 64 (1878).
8. I. M. Klotz, *Diamond Dealers and Feather Merchants. Tales from the Sciences* (Birkhauser, Boston, 1986).
9. B. C. Brodie, *Philos. Trans. R. Soc.* **156**, 781 (1866).
10. W. V. Farrar, *Chymia* **9**, 169 (1964).
11. B. C. Brodie, *Philos. Trans. R. Soc.* **167**, 35 (1877).
12. E. W. Frankland, *Am. J. Math.* **1**, 345 (1878).
13. W. H. Brock and D. M. Knight, *Isis* **56**, 5 (1965).
14. F. A. Matsen, *Adv. Quantum Chem.* **1**, 59 (1964).
15. G. N. Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co., New York, 1923).

16. R. Abegg, Z. Anorg. Chem. 39, 330 (1904).

17 G. N. Lewis, J. Am. Chem. Soc. 38, 762 (1916).

18. W. Kossel, Ann. Phys. 49, 229 (1916).

19. G. N. Lewis, Science 46, 298 (1917).

20. N. V. Sidgwick, Trans. Faraday Soc. 19, 469 (1923).

21. N. V. Sidgwick, The Electronic Theory of Valency (Oxford University Press, London, 1927).

22. L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1939).

23. R. S. Mulliken, Chem. Rev. 9, 347 (1931).

24. J. Van Vleck and A. Sherman, Rev. Mod. Phys. 3, 167 (1935).

25. C. A. Coulson, J. Chem. Soc. 2069 (1955).

26. T. Berlin, J. Chem. Phys. 19, 208 (1951).

27. R. Bader and T. Ngyuen, Adv. Quantum Chem. 14, 63 (1981).

28. R. Bonham, J. Lee, R. Kennerly, and W. St. John, Adv. Quantum Chem. 11, 1 (1978).

29. C. A. Coulson, Rev. Mod. Phys. 32, 170 (1960).

30. H. A. Bent, J. Chem. Ed. 61, 421 (1984).

31. H. A. Bent, J. Chem. Ed. 63, 878 (1986).

32. J. F. Ogilvie, J. Chem. Ed. 67, 280 (1990).

33. J. Simons, J. Chem. Ed. 68, 131 (1991).

34. C. Edmiston, J. Chem. Ed. 69, 600 (1992).

35. J. M. Scott, J. Chem. Ed. 69, 600 (1992).

36. E. R. Scerri, J. Chem. Ed. 69, 602 (1992).

37. J. Simons, J. Chem. Ed. 69, 522 (1992).

38. L. C. Pauling, J. Chem. Ed. 69, 519 (1992).

39. J. F. Ogilvie, in Conceptual Trends in Quantum Chemistry, E. S. Kryachko and J. L. Calais, Eds. (Kluwer, Dordrecht, 1994), p. 171.

40. R. S. Berry, Rev. Mod. Phys. 32, 447 (1960).

41. S. J. Weininger, J. Chem. Ed. 61, 54 (1984).

42. H. Primas, Quantum Chemistry and Reductionism: Lecture Notes in Chemistry Vol. 24 (Springer-Verlag, Berlin, 1981).

43. R. G. Woolley, Adv. Phys. 25, 27 (1976).

44. R. G. Woolley, J. Am. Chem. Soc. 100, 1073 (1978).

45. R. G. Woolley, Struct. Bond. 52, 1 (1981).

46. R. G. Woolley, J. Chem. Ed. 62, 1082 (1985).

47. R. G. Woolley, Chem. Phys. Lett. 125, 200 (1986).

48. R. G. Woolley, Rend. Acad. Naz. Sci. Detta Dei XL, Ser. V, XII, Tom II, Parte II, 35 (1988).

49. R. G. Woolley, in Molecules in Physics, Chemistry and Biology, J. Maruani, Ed. (Kluwer, Dordrecht, 1988), Vol. I, p. 45.

50. R. G. Woolley, in Molecules in Physics, Chemistry and Biology, J. Maruani, Ed. (Kluwer, Dordrecht, 1988), Vol. II, p. 651.

51. R. G. Woolley, J. Mol. Struct (Theochem). 230, 17 (1991).

52. P. Claverie and S. Diner, Isr. J. Chem. 19, 54 (1980).

53. P. Claverie, in Symmetries and Properties of Non-rigid Molecules, J. Maruani and J. Serre, Eds. (Elsevier, Amsterdam, 1983), p. 13.

54. N. D. Mermin, Boojums All the Way Through (Cambridge University Press, Cambridge, 1990).

55. C. Eckart, Phys. Rev. 46, 487 (1934).

56. C. R. le Sueur, S. Miller, J. Tennyson, and B. T. Sutcliffe, Mol. Phys. 76, 1147 (1992).

57. B. T. Sutcliffe, J. Chem. Soc., Faraday Trans. 89, 2321 (1993).

58. B. T. Sutcliffe, in Conceptual Trends in Quantum Chemistry, E. S. Kryachko and J. L. Calais, Eds. (Kluwer, Dordrecht, 1994), p. 53.

59. Z. Makić, Ed., Theoretical Models of Chemical Bonding (Springer-Verlag, Berlin, 1990).