



The source of chemical bonding



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ABSTRACT

Developments in the application of quantum mechanics to the understanding of the chemical bond are traced with a view to examining the evolving conception of the covalent bond. Beginning with the first quantum mechanical resolution of the apparent paradox in Lewis's conception of a shared electron pair bond by Heitler and London, the ensuing account takes up the challenge molecular orbital theory seemed to pose to the classical conception of the bond. We will see that the threat of delocalisation can be overstated, although it is questionable whether this should be seen as reinstating the issue of the existence of the chemical bond. More salient are some recent developments in a longstanding discussion of how to understand the causal aspects of the bonding interaction—the nature of the force involved in the covalent link—which are taken up in the latter part of the paper.

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1. Introduction

According to one familiar story, atomism was finally vindicated after centuries of speculation early in the 20th century with Einstein's and Perrin's work explaining Brownian motion, Bjerrum's explanation of the abnormal specific heat ratio for diatomic molecular gases in terms of the absence of vibrational motion at normal temperatures and other developments associated with the Old Quantum Theory. Shortly after, the first microtheories of the bonding between atoms underlying chemical combination were developed. In the famous 1916 paper in which Lewis indicated how then current insights concerning atomic structure might be adapted to provide a foundation adequate for conceptions of bonding in organic and inorganic chemistry, he set out his notion of ionic and covalent bonds. These involved electrons in the outer shells of combining atoms moving from one atom to the other, in the case of ionic bonding, or forming a shared pair, in the case of covalent bonding, in order that the atoms when combined might be considered to have attained a configuration corresponding to the noble gas element at the end of the corresponding row of the periodic table. Molecules are the result of atoms combining together by forming covalent bonds. This essay describes some key

features of how the understanding of the notion of a covalent bond has developed since Lewis's day.

Although Lewis's conception of a covalent bond as a shared pair of electrons proved fruitful for chemists, especially in the newly developing field of organic reaction mechanisms (Nye, 1993), the fundamental idea was, like Bohr's atom, paradoxical in terms of the classical laws governing the properties of charged particles. How could two negatively charged particles constitute a binding link between two atoms when they should, according to Coulomb's law, repel one another? As with some other paradoxical aspects of atomic particles as conceived in classical terms, the general problem of how a shared electron pair could form a covalent bond was thought to have been solved with the application of quantum mechanical principles soon after the formulation of the new quantum mechanics by Heitler and London (1927). The central idea was to show that the energy of the hydrogen molecule varied as a function of internuclear distance in such a way as to exhibit a deep minimum at the normal bond length. This would show that the most stable arrangement of two hydrogen atoms is as a diatomic molecule, the deep minimum signifying that strong forces come into play acting to restore the equilibrium internuclear distance after any displacement. A conception of the covalent bond arose

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as involving a build-up of electronic charge between the nuclei, allowing the electrons to feel the attractions of both nuclei at the same time and thereby lowering their potential energy. The greater the overlap between the atomic orbitals forming the bond in the internuclear region, the greater the charge build up in this region.

Linus Pauling pioneered the development of quantum chemistry by modulating the approximation procedures necessary for the application of quantum mechanics to molecules in order to interpret the results in terms of the same ideas from the classical structural theory of organic chemistry that Lewis built on and were familiar to chemists. He sought in this way to provide a bridge between classical and quantum chemistry in the form of his Valence Bond (VB) approach, which initially led the majority of chemists to favour his VB method over the quantum mechanically more purist Molecular Orbital (MO) approach developed by Mulliken and others (see [Gavroglu & Simões, 2012](#) for a historical review). But as the MO approach gained the upper hand after the 1960s, largely because of the more tractable calculations that were becoming feasible when formulated in MO terms for ever more complex systems, it seemed that the world of quantum chemistry was becoming ever more foreign to the ideas which chemists had found so useful. In particular, MO theory threatened the classical idea of a bond as a localised material connecting link between specific pairs of atoms in a molecule, which the idea of electron build up between nuclei had seemed to confirm and Pauling had successfully retained in the VB approach. Some main features of these ideas are traced in Sections 2–4, beginning with the initial quantum mechanical treatment of the covalent bond by Heitler and London which put Lewis's covalent bond constituted by a shared pair of electrons on a law-based footing and provided the inspiration for Pauling's VB approach. Mulliken contrasted this atomic point of view with the MO approach, which began from a different starting point:

In the 'molecular' point of view advanced here, the existence of the molecule as a distinct individual built up of nuclei and electrons is emphasized, whereas according to the usual atomic point of view the molecule is regarded as composed of atoms or of ions held together by valence bonds. From the molecular point of view, it is a matter of secondary importance to determine through what intermediate mechanism (union of atoms or ions) the finished molecule is most conveniently reached. It is really not necessary to think of valence bonds as existing in the molecule. ([Mulliken, 1931, p. 369](#))

The procedure of deriving MO descriptions of molecules is outlined in Section 3, illustrated by the ground state electronic configuration of the water molecule. Although this account with its delocalised molecular orbitals bears little resemblance to the classic notion of a structure with two bonds each located between the oxygen and one of the hydrogen atoms, it is possible to give some account of localised bonding on the MO approach, as discussed in Section 4.

But if the MO approach rendered irrelevant the question of what material thing corresponds to the bonds of classical structural theory between atoms in molecules, it facilitated the quest for an explanation of why covalent bonding binds nuclei in a molecule. Although this might be seen as pursuing by "what intermediate mechanism (union of atoms or ions) the finished molecule is most conveniently reached" that Mulliken ascribed only secondary importance in the passage quoted above, it is a pressing question how covalent bonding works. One notion deriving from the VB treatment is that the "exchange" of electrons between atoms explains the bonding in terms of the quantum mechanical treatment

of identical (indistinguishable) electrons—a feature with no classical analogue which is brought into the picture in Section 2 in connection with the Heitler–London theory. Another idea is that binding is electrostatic in origin, arising from the attraction of the shared electron density built up in the bonding region by both nuclei. The development of this idea on the basis of the Hellmann–Feynman theorem is outlined in Section 5. Popular as this explanation is, it has not gone without questioning: "conventional textbooks tend to overemphasize, with respect to all bonds, the importance of electrostatic interaction at the expense of quantum mechanical kinetic effects," ([Bitter, Wang, Ruedenberg, & Schwarz, 2010, p. 238](#)). The line of attack in this passage can be traced back to a suggestion of Hellmann's in the 1930s that was taken up and developed by [Klaus Ruedenberg \(1962\)](#). Although he persuaded some theoreticians to continue with him working in that direction, others were critical, persuaded by a certain application of the virial theorem, and pursued avenues arising from the Hellmann–Feynman theorem. Some of these critics have changed their tune in more recent times and Ruedenberg's ideas have finally taken a stronger hold on the quantum chemical community; these ideas are outlined in Section 6.

The development of ideas in chemistry has not attracted a great deal of interest from philosophers of science in the analytic tradition, and such discussion as there has been on the subject of bonding has largely focused on the question of to what extent the classical notion of a bond has been preserved as MO ideas gained ground at the expense of the VB interpretation. This paper seeks to broaden the picture and introduce some ideas from more recent discussions in the chemical literature to a philosophical audience. The discussion here doesn't by any means do justice to the many facets of the debate. Some main lines of thought are presented, which I hope might inspire others to delve into the wealth of detail and variety of insights in this material. Ruedenberg's line of argument is interesting philosophically because of its modal character. The discussion of what remains of the classical conception of the bond concerns actual molecular wave functions or electron density distributions. Ruedenberg claims that it is not sufficient to consider actual molecular features in order to determine how bonding occurs. Only the bare elements of the strategy can be presented here, and a more detailed discussion must be deferred to another occasion.

2. The first quantum mechanical picture

Chemical atomism was finally vindicated in the late 1920s when the conception of a bond developed within classical structure theory, later understood as the covalent bond arising from a shared pair of electrons described by Lewis, was finally subsumed under the laws of quantum mechanics. Mathematical complexity precluded a rigorous general solution applicable to molecules in general. But the treatment of the simple hydrogen molecule by [Heitler and London \(1927\)](#) seemed to settle the basic principles. In particular, Lewis's shared electron pair bond, understood on the basis of classical principles governing the charge on the electrons, was paradoxical. The electrons should repel one another in virtue of their like charges, and it was totally mysterious how an electron pair could form the basis of an attraction. Lewis himself postulated a restriction on Coulomb's law at small distances, but this was unsatisfactory.¹

Heitler and London devised a method of approximating the exact solution to the hydrogen molecule (a many-body problem with

¹ And, I was first tempted to say, ad hoc. But Lewis's theory was based on J. J. Thomson's partly experimental (dissociation of carbon compounds in cathode tubes didn't display electrical polarity) and largely speculative work on the role of the electron in chemical combination which greatly influenced chemists ([Chayut, 1991](#)). It provided the initial impulse for the school of physical organic chemistry. Further, as Thomson well understood, the restriction on Coulomb's law suggested by Lewis allows for a characteristic length comparable to the size of atoms, which otherwise was a complete mystery.

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