Essay

Gilbert N. Lewis and the Chemical Bond: The Electron Pair and the Octet Rule from 1916 to the Present Day

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We describe the development of Lewis's ideas concerning the chemical bond and in particular the concept of the electron pair bond and the octet rule. We show that the concept of the electron pair bond has endured to the present day and is now understood to be a consequence of the Pauli principle. In contrast the octet rule is now regarded as much less important than was originally generally believed, although Lewis himself knew several exceptions and regarded it as less important than what he called the rule of two (the electron pair). The octet rule was more strongly promoted by Langmuir who is also responsible for the term covalent bond. However, many more exceptions to the octet rules than were known to Lewis are now known and the terms hypervalent and hypovalent used to describe such molecules are no longer particularly useful. Today it is realized that bonding electron pairs in many molecules are not as well localized as Lewis believed, nevertheless resonance structures, i.e., plausible alternative Lewis structures, are still often used to describe such molecules. Moreover electrons are not always found in pairs, as for example in linear molecules, which can, however, be satisfactorily described by Linnett's double quartet theory. The electron density distribution in a molecule can now be analyzed using the ELF and other functions of the electron density to show where electron pairs are most probably to be found in a molecule.

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Key words: G. N. Lewis; chemical bond; electron pair; octet rule

Introduction

This year (2006) marks the 90th anniversary of the publication of G. N. Lewis's 1916 paper entitled "The Atom and the Molecule."[1] This remarkable and revolutionary paper laid the foundation for much of our present day understanding of two fundamental concepts of chemistry: The chemical bond and molecular structure. It was, without a doubt, one of the most influential chemistry papers ever published. His ideas were treated more fully and in greater detail, and applied to a wide range of substances and their reactions in his book "Valence and the Structure of Atoms and Molecules," published in 1923.[2] The enormous influence he has had on our understanding of these two essential concepts of chemistry is only equaled by that of Linus Pauling, who acknowledged his great indebtedness to Lewis by dedicating his famous book "The Nature of the Chemical Bond" to him.[3]

Lewis's most important ideas were the rule of two (the electron pair), including the essential concept that a single bond consists of a pair of electrons shared between the valence shells of the two bonded atoms, and the rule of eight (the octet rule). Subsequently it has become clear that there are exceptions to both rules, particularly the octet rule, nevertheless the rule of two (the electron pair) remains the foundation for much of our present understanding of the chemical bond and molecular structure. In contrast, although the octet rule was of great importance when it was first proposed, its usefulness today is considerably diminished.

The purpose of this article is to describe the development of Lewis's ideas concerning the chemical bond and in particular the rules of two and eight; to discuss how more recent work has been built on his ideas; to show that his most important idea, the electron pair has endured to the present day; and to discuss how his ideas have sometimes been misunderstood, or misapplied, so as to lead to controversial and often meaningless, and unnecessary discussions.

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To fully appreciate Lewis's monumental achievement, it is important to remind ourselves about the state of knowledge at the time, and how much of it was relatively new or contemporary with his own research on chemical bonding. From the start of the 19th century, chemical knowledge was becoming substantial, through, for example the acceptance of Dalton's atomic theory, many additions to the number of known elements, the gradual accumulation of new experimental results about the compositions of substances, their formulas, reactions, and reactivities. Even though static electricity had been known from the early 17th century, and Coulomb's law dates from 1784, it was not until the discovery of the voltaic pile to generate an electric current that Humphrey Davy could in 1806 perform his many electrolysis experiments, including, for example, the preparation for the first time of elemental sodium and potassium from their molten salts. This work demonstrated that an electrical current could break the bonds between the atoms in a compound strongly suggesting that chemical bonding is electrical in nature, an idea that Newton had postulated in 1718. During the last half of the 19th century it had become clear that the atoms in molecules were held together by a force, apparently acting in the vast majority of cases, between pairs of atoms and chemists had drawn a line between such atoms and called it a bond. This convention was first used by Couper in 1858 and shortly after by Crum-Brown in 1861 as discussed in references 4a and 4b. Strictly speaking, such a line is simply a way of representing the concept of a bond, because a bond is the word that chemists use to express the idea that two atoms are held strongly by a constraining force, but of course, a bond has no physical reality. Hendry[5] quotes Coulson as saying "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 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."

In the same era, it was also becoming clear that the atoms of a particular element form a characteristic number of bonds, which was called its valence, and that bonds, particularly those of carbon, are formed in specific directions. So, even though none of the powerful methods of direct molecular structure determination were available before the discovery by von Laue of X-ray diffraction and its use in 1912 in determining crystal structures[6] chemists had been able to work out the structures, that is to say the pattern of the bonding, in a very large number of organic molecules. Structural organic chemistry had become a well established subject well before the first use of X-rays to determine crystal structures and well before Lewis published his ideas. This great achievement was made at a time when there was very little understanding of the composition and nature of atoms. However, despite the great usefulness of the concept of a bond, the type of force holding the atoms together, particularly in organic molecules, was still a mystery.

Since the discovery of the electron by J. J. Thompson in 1897 and his proposal of a model of the atom as consisting of electrons embedded in a uniform sphere of positively charged matter, it had come to be accepted that electrons must be involved in bonding. In crystalline inorganic salts, the forces holding the crystal together were believed to be the electrostatic forces between oppositely charged ions. Although attempts were made to use this model to explain the bonds in organic molecules, it was quickly realized that this was not possible and that these bonds, and those in many inorganic molecules, were of a different kind, later called covalent bonds. Such was the state of knowledge when Lewis made his first proposals concerning the structure of the atom and the nature of the chemical bond.

The Electron Pair and the Rule of Eight

As early as 1902 when attempting to explain the ideas involved in the periodic law and Mendeleev's periodic table (1871) to an elementary class in chemistry and intrigued by the recently suggested model of the atom based on J. J. Thomson's discovery of the electron in 1897, Lewis devised his own model (see page 29 of Ref. 2). But, although he used it in his teaching he did not publish it at that time. It was not until 1923 that he reproduced his 1902 sketches in his book.[2] He proposed that following helium with a valence shell of two electrons, the electrons were located in successive shells containing up to eight electrons arranged at the corners of a cube. A valence shell of eight electrons appeared to be a particularly stable arrangement as it was the valence shell electron arrangement for each of the other inert (noble) gases, which had been discovered by Ramsay in the period 1894–1898. Although it was clear that by transferring electrons between atoms to form ions the formulas of many crystalline inorganic compounds could be accounted for, Lewis was at that time unable to account for the nature of the bonds in organic molecules and inorganic molecules such as H_2,Cl_2, P_4, and S_8, or to explain the nature of the bonds in these molecules. So he did not further develop his ideas until a 1913 paper[7] and his famous and revolutionary 1916 paper[1] by which time the nuclear model of the atom proposed by Rutherford in 1910 had become generally accepted. In the 1913 paper, he had classified a large number of substances according to their physical properties as polar or nonpolar, in which salts were characterized as very polar at one end of the scale and hydrocarbons at the other end were nonpolar. How then to find a single model that would account for the bonding in this huge variety of substances? In his 1916 paper, inspired by the fact that the vast majority of stable molecules have an even number of electrons, he proposed that the electrons in a molecule are paired together and that a chemical bond consists of a pair of electrons shared between two atoms. In this way he was able to simply explain valences and the formulas of a very large number of molecules. By "shared" he meant that a single pair of electrons could be considered to occupy the valence shells of both the bonded atoms. He noted that this concept also led to the great majority of atoms in molecules, except hydrogen having a valence shell of eight electrons and in particular four pairs, that is to say a noble gas valence shell, just as is found in the outer shell of many stable ions such as Na^+, Al^{3+}, and Cl^-. He called this the rule of eight. However, Lewis was not able to explain, neither why it appeared that electrons have a special ability to form pairs, even though electrons repel each other, nor why two electrons could form a bond between atoms. Nevertheless, he was so convinced

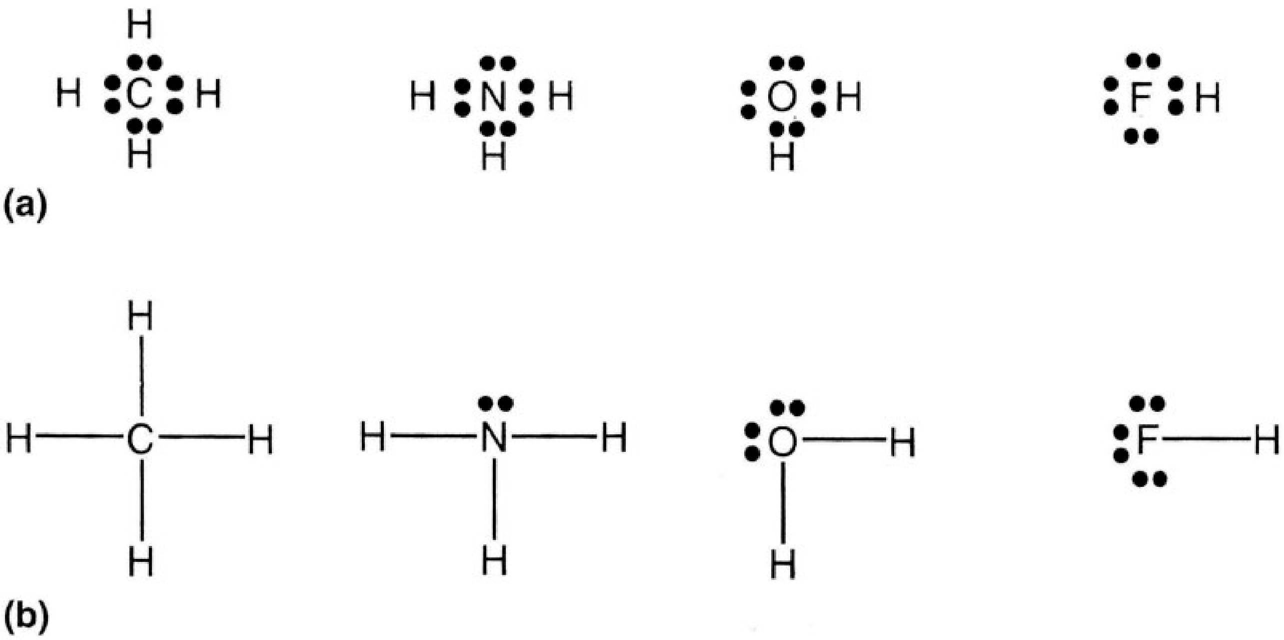


Figure 1. Lewis structures.

that the electron pair was the clue to understanding the chemical bond, as indeed it is, that he postulated (incorrectly as it turned out) that Coulomb's law was invalid for very short distances. Indeed, the Lewis electron pair has continued to be a most important concept in chemistry that can now be justified and understood in terms of quantum mechanics and, in particular, the Pauli principle. In his 1916 paper he wrote, for the first time, structures such as those illustrated in Figure 1, which introduced pairs of dots to represent electron pairs. Electronic structures written in this way or with a line representing a bond or shared pair have become very familiar and have long been known as Lewis structures.

In his 1916 paper he suggested that if the eight electrons that he originally depicted as having a cubic arrangement were drawn into pairs at the center of each of four sides of the cube to form a tetrahedral arrangement, this model could immediately account for the known tetrahedral geometry of CX_4 molecules. He also pointed out that although the cubic arrangement of electrons could explain the single and double bonds in terms of the sharing of edges and faces of two cubes, it could not explain the triple bond, whereas both double and triple bonds could be accounted for by the sharing of edges and faces of two tetrahedra of electron pairs. This model also correctly predicted the planar geometry of ethene and the linear geometry of ethyne and was consistent with earlier pictures that used bent bonds to depict such molecules[8] (Fig. 2). This model could also account for the free rotation of groups about single, but not about double bonds.

At about the same time as Lewis's paper was published in 1916, Kossel[9] noted that stable ions of the main group elements (except Li^+, Be^{2+}) have the same electron arrangements as the inert gases, so in a sense he discovered the octet rule for ionic compounds, although he said nothing about the shared pair and the octet rule for covalent compounds. He recognized that atoms that did not have noble gas arrangements tended to gain or lose electrons to obtain the same number of electrons as an inert gas. Thus he could explain ionic compounds but not covalent molecules. This was left for Lewis.

Today, when we are so familiar with Lewis structures, it is difficult to imagine the enormous impact of Lewis's ideas. But the extent to which they clarified molecular formulas and chemical bonding led to their very rapid adoption by the chemical community. For example, they were used in an introductory textbook for students as early as 1919.[10] Lewis recognized that there was an apparent disagreement between his static model of the atom and the Bohr theory of electrons rotating in orbits proposed in 1913. But by 1923, he thought that these two apparently conflicting theories might be reconciled by assuming that

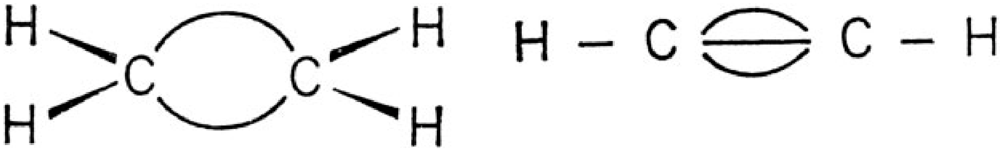


Figure 2. Bent bond descriptions of ethene and ethyne.

the orbit of each electron had a fixed orientation in space and that its average position in the orbit corresponded to its position in his static model.[2] Lewis then speculated that because of the orbital motion of an electron it would have a magnetic moment that could be oriented in the same or opposing directions. Electrons with their moments opposed would be expected to attract each other to form pairs. However, it is now known that magnetic forces arising from either orbital motion or spin are too weak to account for electron pairing.

A few years after Lewis's 1916 paper, Langmuir published a long paper[11] in which he enlarged on Lewis's ideas while acknowledging that Lewis's work had been the basis and inspiration for his own work. He accepted the rule of eight, which he renamed as the octet rule and the shared electron pair bond, which he renamed as the covalent bond. He also suggested that the attraction between oppositely charged ions should be called an electrovalent bond (now called an ionic bond) to clearly distinguish this type of bonding from that due to the sharing of an electron pair. However, he ignored Lewis's tetrahedral arrangement of four pairs and returned to Lewis's original cubic arrangement. He knew that this could account for single and double bond formation by the sharing of two corners or two edges of two cubes but failed for triple bond formation, for which he invented a quite different and rather exotic model, which was never generally accepted. A major part of this paper was, however, devoted to developing an entirely speculative model of the electronic arrangements of the elements beyond scandium, which, he postulated, were based on larger and more complicated electron arrangements than the cube. These complicated models soon faded into obscurity. For the elements of periods 2 and 3, Langmuir placed much more emphasis on the octet rule than Lewis, who admitted that there were exceptions, such as the molecules BCl_3 and PCl_5, and who considered the electron pair, which he also called the rule of two, to be more important than the rule of eight. In short, Langmuir, who was a popular and convincing lecturer and introduced the terminology that we use today, did much to promote Lewis's ideas, but did not do much to improve upon or extend Lewis's two important ideas, so it is only fitting that Lewis is considered to be the originator of the electron pair bond and the octet rule. Bancroft[12] once said "Langmuir is the most convincing lecturer I have ever heard. I have heard him talk to an audience of chemists when I knew that they did not understand one-third of what he was saying; but thought they did. It is very easy to be swept of one's feet by Langmuir." Lewis appears to have been somewhat antagonistic to Langmuir apparently believing that he had stolen his ideas, or at least had not properly acknowledged them. It seems probable also that Lewis did not establish friendly relations with Langmuir because of the difference in their temperaments. Langmuir was a much more flamboyant and extrovert person than Lewis, who was quieter and more reserved. In his 1923 book Lewis said "In my original paper, I contented myself with a brief description of the main results of the theory, intending at a later time to present the various facts of chemistry, which made necessary these radical departures from the older valence theory. This plan, however, was interrupted by the exigencies of war, and in the meantime the task was performed by Dr. Irving Langmuir in a brilliant series of some twelve articles, and in a large number of lectures given here and abroad. It is largely through these papers and addresses that the theory has received the wide attention of scientists. It has been the cause of much satisfaction to me that in the course of this series of applications of the new theory, conducted with the greatest acumen, Dr. Langmuir has not been obliged to change the theory that I advanced. Here and there he has been tempted to regard certain rules or tendencies as more universal in their scope than I considered them to be in my paper, or than I now consider them . . . The theory has been regarded in some quarters as the Lewis–Langmuir theory, which would imply some sort of collaboration. As a matter of fact, Dr Langmuir's work has been entirely independent."

Unfortunately, Lewis was slow after the 1914–1918 war in following up his 1916 paper, with other publications enlarging on his original ideas as he had intended to and finally did in his book in 1923. But there were good reasons for this: his war service and his work in thermodynamics. In December of 1917 he was appointed director of the Chemical Warfare Service Laboratory in Paris and served in this position during 1918. And then he was very busy continuing his work on thermodynamics with Randall and preparing the publication of another masterpiece "Thermodynamics and the Free Energy of Chemical Substances" also published in 1923.[13] Fortunately, the clarity of his arguments and the wide scope of his book[2] made it very successful and ensured that his ideas were widely accepted so that he became generally recognized as the discoverer of the rule of two (the electron pair) and the rule eight (the octet rule).

It is important to bear in mind that the octet rule is just a rule based on empirical observations. But, partly at least because of Langmuir's vigorous promotion, the octet rule came to be regarded more as a fundamental law of nature that should have no exceptions. And this misunderstanding of the octet rule has prevailed into recent times, despite the existence of molecules such as PCl_5 and SF_6, which were regarded by Lewis as exceptions to the octet rule, because they have five and six electron pairs respectively in the valence shell of the central atom. Such molecules with more than four electron pairs in the valence shell of the central atom have been considered to belong to a special class of molecules called hypervalent, with bonds that have been believed to be different from those in "ordinary" molecules as we will discuss in a later section "Electron Pairs are Not Always Well-Localized." This overemphasis on the octet rule may reasonably be said to have delayed until 1962 the discovery of the noble gas molecules, which clearly do not obey the octet rule.[14] Lewis was not only responsible for the rule of two (the electron pair) and the rule of eight (the octet rule) but also for the beginning of the understanding of molecular geometry when he proposed that the electrons in an octet are arranged in pairs at the corners of a tetrahedron, so that CX_4 molecules would have a tetrahedral structure, in agreement with the 1824 proposals of van't Hoff and leBel.[15] But he also appreciated that this model implied that NX_3 molecules with one unshared (lone) pair should have a triangular pyramidal shape and OX_2 molecules with two lone pairs an angular shape even though at the time there was no experimental evidence for these proposed structures, such as the evidence provided by the optical activity of chiral molecules of the type $CX_1X_2X_3X_4$ for the tetrahedral geometry of the bonds formed by carbon.

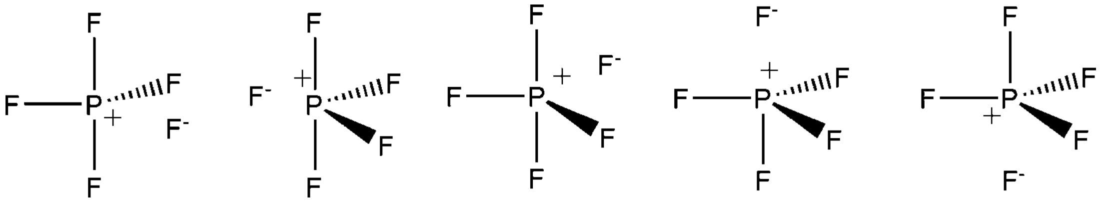


Figure 3. Ionic–covalent resonance structures for PF_5 postulated to suggest that PF_5 obeys the octet rule.

Mainly because only a small number of molecules with more than four electron pairs in the valence shell of an atom were known at the time, and their structures in many cases were not known, there was little interest in trying to explain their geometries until the work of Sidgwick and Powell in 1940[16] by which time more examples had been discovered and their structures determined. They pointed out that the geometry of very many molecules appears to depend on the total number of electron pairs in the valence shell of the central atom whether this was two, three, or four, or five, six, seven, or even eight, and that the unshared (lone-pairs) play a vital role in determining the geometry of all the molecules of groups 14–18 as Lewis had suggested for octet molecules. Their work led to the VSEPR model in 1957.[17–19]

In the following sections, we describe how ideas concerning the octet rule and the electron pair have been modified over the years.

Exceptions to the Octet Rule

Lewis was well aware that there are exceptions to the rule of eight, as are exemplified, for example, by PF_5, for which the Lewis structure has ten electrons in the valence shell of phosphorus, and by BCl_3 for which the Lewis structure has only six electrons in the valence shell of boron. However, as we have already pointed out, the belief in the octet rule became so strong over the years, partly due to Langmuir's vigorous promotion of the rule, and partly because exceptions were rather few until more recent times, that it came to be regarded as a fundamental law of nature rather than as an empirical rule. Thus molecules that do not obey the octet rule came to be regarded as exceptional and the special terms hypervalent and hypovalent were invented to describe them. Reluctance to give up familiar and apparently well established ideas in the face of contrary experimental facts has often led to the invention of new, and sometimes unnecessary, concepts in an attempt to retain the old ideas. Thus, attempts have been made to formulate these exceptions to the octet rule in such a way that they appear to obey the rule, but such concepts become unnecessary once it is recognized that the octet rule as formulated by Lewis is not a law of nature but simply an empirical rule to which there are exceptions. Indeed the octet rule applies strictly only to the period 2 elements, C, N, O, and F. For the atoms of all other elements the rule may or may not be obeyed.

Hypervalent Molecules

Although the molecules of the period 3 elements often obey the octet rule, as in molecules such as PF_3 and SF_2, the Lewis structures of AX_5 and AX_6 (and related molecules such as AX_4E and AX_5E) show they may have up to 12 electrons in their valence shell and do not therefore obey the octet rule. Lewis had stated clearly that bonds may be partially ionic and that the electron pair might be unequally shared depending on the electron-attracting properties (what we now call the electronegativies) of the two bonded atoms, but nevertheless according to Lewis, such unequally shared pairs contributed fully to the valence shells of both bonded atoms. Nevertheless following a suggestion by Pauling,[3] the structures of hypervalent molecules such as PF_5 are sometimes written with resonance (Lewis) structures involving ionic bonds, as in the structures for PF_5 in Figure 3, so as to appear to conform to the octet rule. These structures were interpreted to mean that in each Lewis diagram (resonance structure) there is a single fully ionic bond and four fully covalent bonds and that therefore the octet rule is obeyed. This interpretation is incorrect because such structures really imply that there are five partially ionic bonds, in other words five unequally shared electron pairs and so the octet rule as formulated by Lewis is not obeyed. Lewis considered that a molecule such as CF_4, in which the bonds are polar, and the four electron pairs are therefore unequally shared, obeys the octet rule. So it follows logically that a molecule such as PF_5 does not obey the octet rule. Indeed there has been a rather widespread misunderstanding that the octet rule means that if there is the equivalent of four fully shared electron pairs in the valence shell of a central atom A, then the molecule obeys the octet rule. Although the resonance structures involving ionic bonds are consistent with the expected polarity of the P—F bonds, there is no justification for choosing just these particular resonance structures to represent the molecule other than that they do so in a way that superficially appears to obey the octet rule.

The 3 center–4 electron bond model has frequently been used to describe the bonding in hypervalent molecules, particularly for the axial bonds in trigonal bipyramidal molecules such as PF_5. But this description has been controversial and it has been argued that it is simply equivalent to two very polar 2-electron bonds.[19] Indeed this is the conclusion reached in a recent extensive and detailed theoretical study.[20]

In more recent times, attempts have been made to calculate the number of electrons in the valence shell of a hypervalent molecule but the results vary with the method of calculation used.[21,22] When this number was found to be close to eight, or more often significantly smaller than eight, it was claimed that these molecules obey the octet rule. This conclusion is, however, incorrect, as the octet rule takes no account of polarity, and counts partially shared electron pairs equally with fully shared pairs. Moreover, other calculations have shown that in some molecules with weakly electronegative ligands such as As(CH$_3$)$_5$, the number of electrons in the valence shell of the central atom is more than eight.[23] So even in the incorrect sense that an atom with fewer than eight electrons in its valence shell obeys the octet rule, these particular molecules do not obey the octet rule.

Hypovalent Molecules

Molecules with fewer than eight electrons in the valence shell of a central atom have been called hypovalent, in analogy with hypervalent. Any molecule with three or fewer singly bonded ligands and no lone pairs is necessarily hypovalent. As in the case of hypervalent molecules, resonance structures have been invented for hypovalent molecules in an attempt to show that they also really obey the octet rule. Again following Pauling,[3] the bonding in the molecule BF$_3$ is often described as involving an important contribution from three resonance structures in each of which there is a B=F double bond and in which the boron atom therefore has an octet (Fig. 4).

Another justification given for these structures is that, in the simple valence bond structure with three single bonds formed from three sp^2 orbitals on boron, there is an empty 2p orbital, which it has been assumed is occupied by electrons from the F ligands. But there is no convincing evidence that justifies this assumption. The shorter length of the BF bond (131 pm) in BF$_3$ than in BF$_4^-$ (138 pm) is often cited as evidence of double bond character, but the short length can be equally well justified by the fact that three ligands can pack more closely around a central atom than four.[19,24]

The octet rule strictly only applies to the atoms of the elements C, N, O, and F of period 2. The atoms of the corresponding elements in periods 3 and beyond may obey the octet rule but not necessarily in all their molecules.

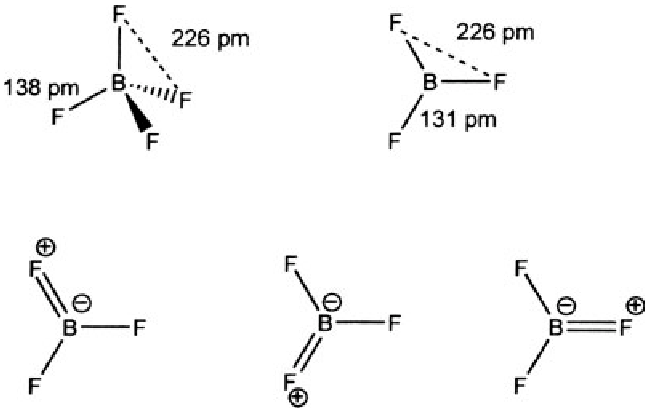


Figure 4. Top line: The interligand distances in BF$_3$ and BF$_4^-$ are equal, showing that the shorter bonds in BF$_3$ could be due to the closer packing of the ligands in BF$_3$ than in BF$_4^-$. Bottom line: Resonance structures for BF$_3$ purporting to show that BF$_3$ obeys the octet rule.

Electron Pairs are Not Always Well-Localized

Lewis proposed that all the electrons in molecules with an even number of electrons are present in localized pairs. However, it is well known that some molecules, such as the benzene molecule, cannot be well represented by a single Lewis structure, because the electron pairs are not well-localized as a Lewis structure implies. Pauling[3] showed, however, that such molecules can be satisfactorily described by a linear combination of two or more such Lewis structures, which he called resonance structures. This combination, called a resonance hybrid, has a lower energy than any of the contributing structures. To describe the benzene molecule, the two Kekulé structures are usually selected as resonance structures but for a more accurate structure other resonance structures may be added. Resonance structures have become a common method for describing the bonding in molecules in which at least some of the electrons are not well-localized into bonding or nonbonding pairs, because the familiar and useful Lewis structures can be retained as a basis for a description of the bonding. However, the resonance structure description of a molecule becomes increasingly less useful as the number of delocalized electrons in the molecule increases, and a molecular orbital description, in which electron pairs are assigned to delocalized orbitals that cover the entire molecule, then becomes correspondingly more useful.

Electrons Do Not Always Form Pairs: Linnett's Double Quartet Theory

Lewis believed that electrons in molecules with an even number of electrons are always paired together. In his book[2] he stated that "the simplest explanation of the predominant occurrence of an even number of electrons in the valence shells of molecules is that the electrons are definitely paired with each other." He proposed that: "Two electrons thus coupled together, when lying between two atomic centers, and held jointly between the two shells, I have considered to be the chemical bond." In his structures, he showed all the electrons, including the nonbonding electrons, as pairs. Subsequently, and up to the present day, all Lewis structures are written in this way. Nevertheless, we now know that in some molecules, even those with an even number of electrons, some of the electrons are not paired because, in fact, electrons by themselves have no tendency to form localized pairs. Indeed they repel each other electrostatically and so should keep apart, which was the reason that Lewis originally assumed that Coulomb forces did not operate between electrons at very short distances.

In 1925, shortly after the publication of Lewis's 1923 book, it was discovered that the electron has spin (a property that can be described by a spin quantum number that can have only two values). In the same year, Pauli proposed his famous principle: The wave function for an electronic system must be antisymmetric to the exchange of two electrons. The important physical consequence of this principle is that electrons of the same spin keep as far apart as possible. The behavior of electrons in molecules is thus determined by two properties; charge correlation—the effect of their mutual electrostatic repulsion, and spin correlation—the consequence of the Pauli principle. But the impor-

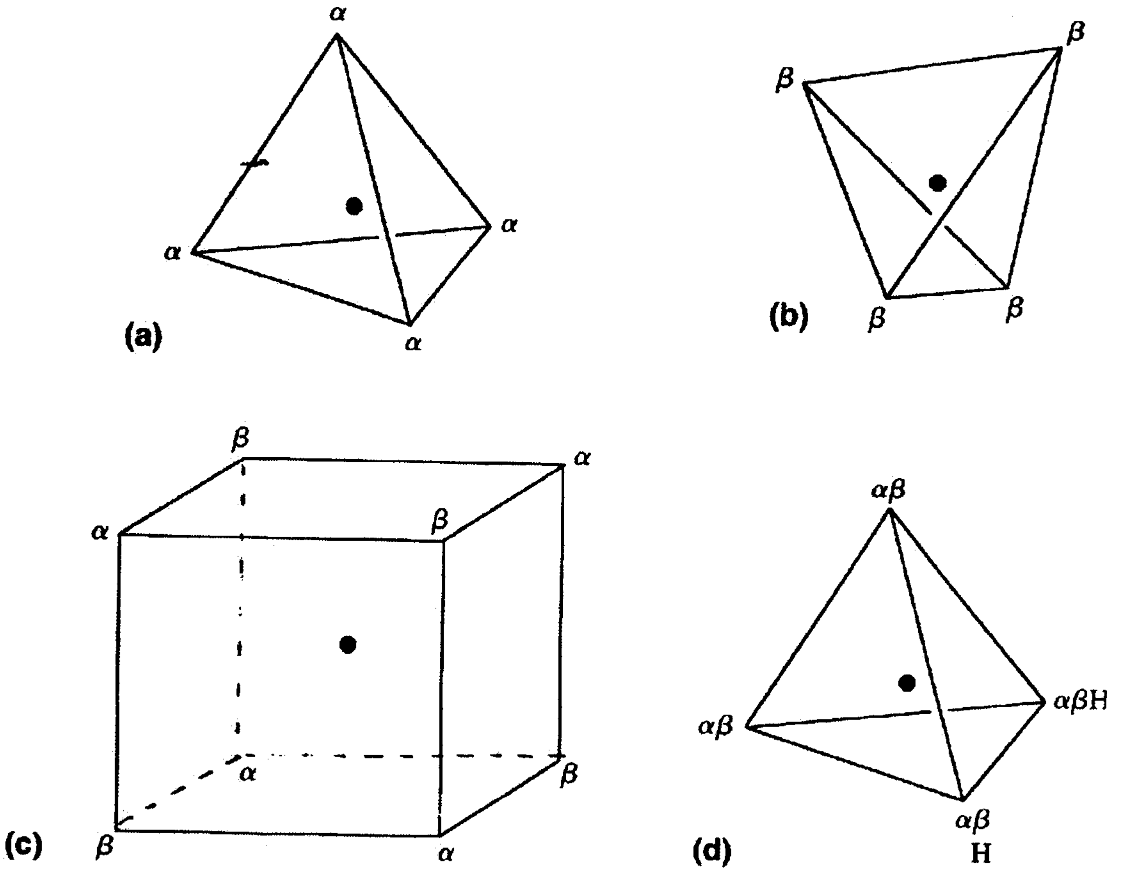


Figure 5. Most probable positions of the electrons in a valence shell octet and the localization of these electrons into pairs in the water molecule.

tance of spin correlation for understanding when and why electrons form pairs in molecules was not understood until the work of J. E. Lennard-Jones in the 1950s.[25] He showed that in a valence shell octet such as that of neon the most probable relative location of four electrons of the same spin is at the corners of a tetrahedron. So there are two sets of electrons each with their most probable locations at the corners of a tetrahedron (Fig. 5).

In 1961, Linnett published an important paper[26] that followed up Lennard-Jones's work and he followed this paper in 1963 with his book "The Electronic Structure of Molecules."[27] He called each of the two same-spin sets of four electrons a double quartet, and he emphasized that electrons in molecules are not always paired as Lewis had proposed. Following Lennard-Jones, he pointed out that as a consequence of spin correlation, the valence electrons in neon and related ions with an octet will have four electrons of the same spin with a most probable arrangement at the corners of a regular tetrahedron and the other four electrons of opposite spin will have their most probable arrangement at the corners of another tetrahedron (Fig. 5). And the two tetrahedra will be kept apart by charge correlation, giving an overall most probable relative arrangement of eight electrons with alternating spins at the corners of a cube which, of course,

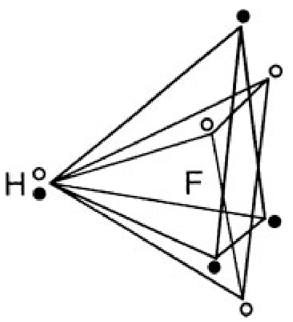


Figure 6. Most probable positions of the electrons in the HF molecule.

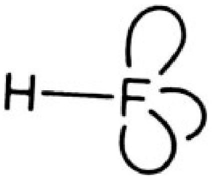


Figure 7. Valence bond model of the HF molecule showing the localized orbitals of the nonbonding electrons, each containing a pair of electrons.

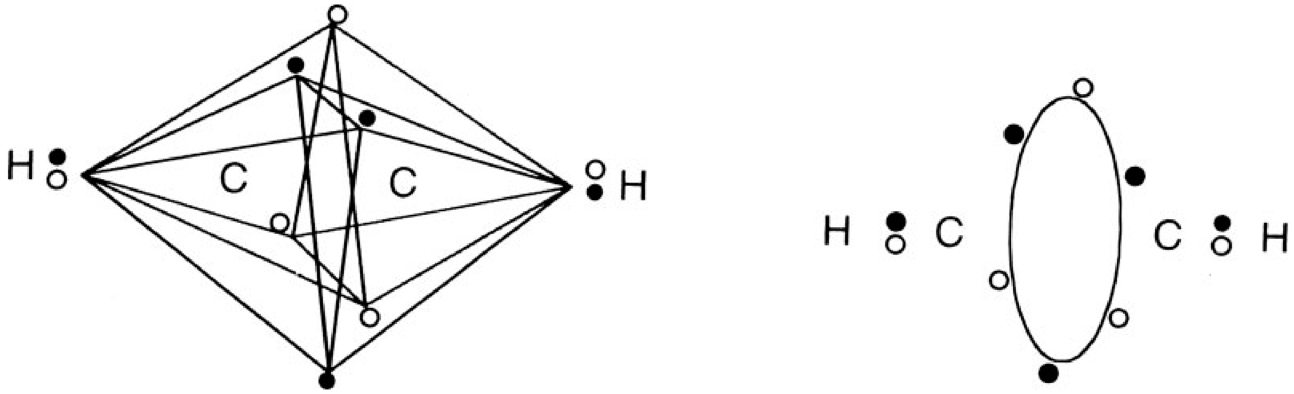


Figure 8. Double quartet model of the bonding in the ethyne molecule.

is the arrangement originally suggested by Lewis, who had no knowledge of electron spin. According to this picture, there are no localized electron pairs in a free atom or ion with an octet of electrons. Localized electron pairs are formed in molecules only as a consequence of the attraction provided by the positively charged cores of the other atoms in the molecule. For example, in the HF molecule, the two tetrahedra around each F atom are brought into coincidence at one corner by the presence of the hydrogen nucleus to form the H—F bonding pair, but there are no other cores to localize the remaining six electrons into pairs (Fig. 6). In contrast, in the H_2O molecule, the presence of the two cores of the hydrogen atoms is sufficient to form four localized pairs—two bonding and two nonbonding. However, molecules such as HF have continued to be pictured using Lewis structures showing all the electrons in pairs. This is no doubt, at least partly, a consequence of the popularity of the valence bond or localized orbital theory in which the Pauli principle is stated in the form that an orbital cannot contain more than two electrons, which must be of opposite spin. So a molecule such as HF has been very commonly depicted as having four approximately tetrahedral sp^3 orbitals centered on the fluorine atom, each containing a pair of electrons, or often more simply with a bond and three lone-pair lobes at the back of the F atom (Fig. 7). In general, the nonbonding electrons in any singly-bonded atom are not paired.

Other molecules in which some of the electrons are not paired include triply-bonded linear molecules such as ethyne, in which the most probable positions of the electrons of the triple bond are not paired but are distributed in a circle surrounding the molecular axis (Fig. 8).

An important advantage of Linnett's theory is that it depicts the ground state of the O_2 molecule in a way that shows it to be a paramagnetic diradical, which is of course not shown by the conventional Lewis diagram, or by the VB model, in which the pairing of all the electrons is assumed. In the Linnet picture, there are seven electrons of one spin and five of opposite spin, none of which form close pairs (Fig. 9). The acceptance of this model for the oxygen molecule would have served to refute claims that the MO theory provides the only valid description of the bonding in the O_2 molecule. It is, indeed, superior to the VB theory because the valence bond theory, which assumes that all the electrons in a molecule are paired, cannot account for the paramagnetism of oxygen. In contrast, Linnett's double quartet theory avoids this problem by not requiring that electrons are always paired and so it provides an equally valid alternative to the MO theory.

Odd electron molecules, which Lewis recognized are exceptions to the octet rule and which he correctly predicted should be paramagnetic, are also easily described by the Linnett double quartet model. For example, according to the double quartet model, the NO molecule has five electrons of one spin and six of the opposite spin, which will have the most probable arrangement shown in Figure 9. There are five shared bonding electrons and three nonbonding electrons on each atom, so that each atom satisfies the octet rule.

It is unfortunate that Linnett's work has never received the recognition that it deserves. The difficulty of representing the electronic structures of these molecules in any simple way probably accounts, at least partly, for the lack of popularity of the double-quartet theory. Linnett devised a method using thick

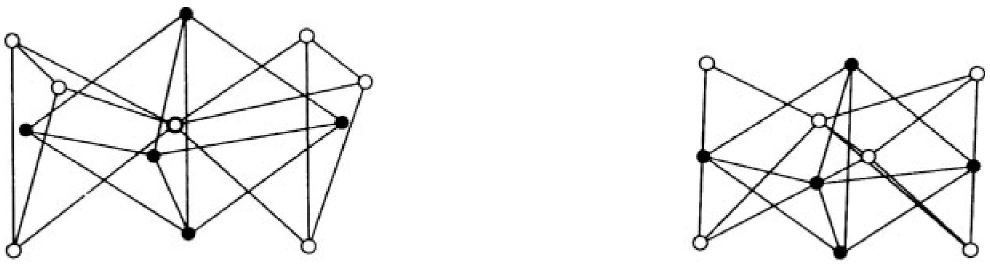
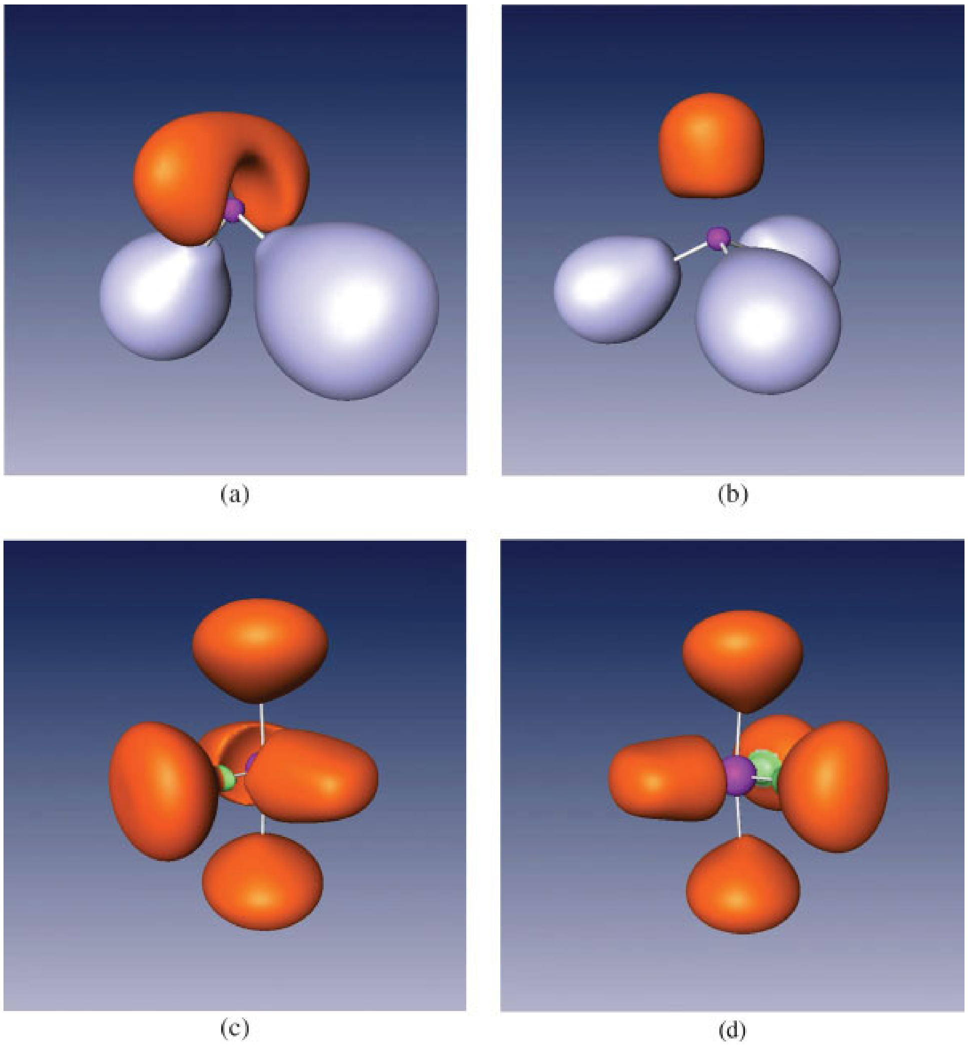


Figure 9. Double quartet model of the bonding in the O_2 and NO molecules.



(a) (b)

(c) (d)

Figure 10. Isosurfaces of the electron localization function ELF for H_2O, NH_3, and ClF_3 showing the core purple, monosynaptic (lone pair) brown, and disynaptic (bonding) green, monosynaptic (CH) blue, basins corresponding to the qualitative domains of the VSEPR model.

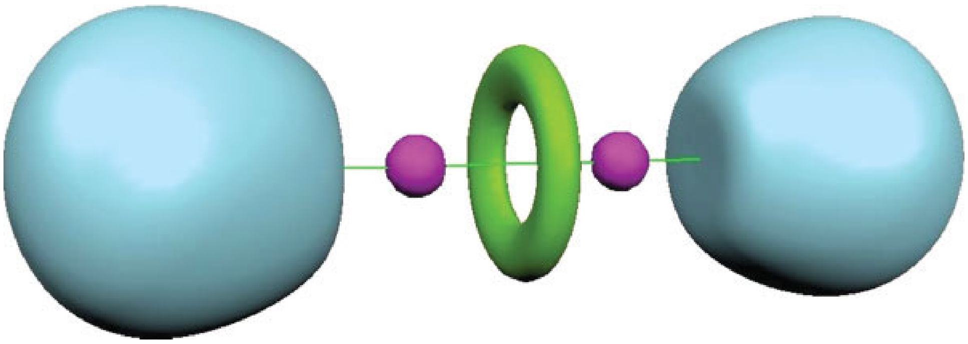


Figure 11. Isosurfaces of the ELF for ethyne: Disynaptic (CC bonding) green and monosynaptic (CH) blue.

bond lines to represent localized pairs of opposite spin electrons and thin lines to represent opposite spin electrons that are not paired, but this representation is rather clumsy and difficult to understand when used for molecules other than diatomics.

The Classical Electron Pair and the Electron Pair Today

A subject of much discussion at the time of Lewis's publications was the apparent conflict between the chemist's static picture of the atom as developed by Lewis, in which electrons were assumed to be in fixed positions, and the picture of the atom developed by Bohr. To Lewis and other chemists at the time, the relatively rigid structure of the majority of molecules and the fixed directions of bonds in space appeared to imply that the electrons involved in bonding must also be fixed in position. Yet this conflicted with the Bohr theory of electrons rotating around the nucleus in circular or elliptical orbits.

Today both the model of electrons in fixed positions and the Bohr model have been superseded. Because of the uncertainty principle, we can only determine the probability of finding electrons at any given position in an atom or molecule, which is conveniently expressed in terms of the electron density. It is the electron density of a molecule that is static even though all the electrons are in rapid motion. From Lewis's static model in which he pictured a bonding electron pair in a bond as being situated at some point between the two bonded atoms, it might be anticipated that the electron density would be a maximum at the position of the bonding pair of electrons but this is far from the case. In all molecules, the electron density is strongly concentrated around each of the nuclei and reaches a maximum at each nucleus as shown and nothing in the electron density shows the presence of electron pairs.

However, it is not the total density that is of most interest for many purposes but rather the most probable positions of localized electron pairs as determined by the Pauli principle. These positions can be found in a qualitative way on the basis of the assumption that the most probable positions of electron pairs are as far apart as possible. This assumption is the basis of the VSEPR model.[17–19] These positions can be found more exactly by a suitable analysis of the electron density such as that provided by the electron localization function (ELF).[28–30] This function exhibits maxima at the most probable positions of localized electron pairs and each maximum is surrounded by a basin in which there is an increased probability of finding an electron pair. These basins correspond to the qualitative electron pair domains of the VSEPR model and have the same geometry as the VSEPR domains. There are two main types of basin: disynaptic basins, which are connected to two atomic cores and correspond to bonding domains, and monosynaptic basins, which qualitatively correspond to nonbonding or lone pair domains as can be seen by the examples in Figure 10. The population of each of these basins can be determined by integration of the electron density over the volume of the basin and in each case is close to two electrons.

The ELF is also consistent with the Linnett double quartet theory. In a molecule such as C_2H_2, there are not three disynaptic basins corresponding to three localized electron pairs between the carbon atoms but a single disynaptic basin with a toroidal shape containing all six nonbonding electrons (Fig. 11). Similarly in ClF_3 (Fig. 10), in addition to the the disynaptic Cl—F basins and the two monosynaptic basins in the Cl valence shell, there is a single toroidal-shaped monosynaptic basin "lone-pair" basins at the back of each F atom corresponding to the Linnet double quartet model rather than three monosynaptic expected from the Lewis model.

Summary and Conclusions

The Electron Pair

That electrons in molecules form localized pairs (the rule of two) and that a shared pair constitutes the chemical bond, thus completing the valence shells of the two bonded atoms was postulated by Lewis in 1916 at a time when there was considerable uncertainty about the nature of the chemical bond, particularly the covalent bond in organic molecules. This simple, but brilliant proposal immediately revolutionized chemistry because for the first time the structures of the majority of molecules and their bonding became very clear and Lewis's model was quickly and widely adopted. It is remarkable that the electron pair and Lewis structures have survived for 90 years as very useful concepts despite the advent of quantum mechanics about 10 years after the publication of Lewis's 1916 paper. The reason is clear: although electrons are not localized in space as the Lewis model supposes, the most probable positions of opposite spin pairs are indeed localized because of the Pauli principle and are just those proposed by Lewis and the VSEPR model. Consequently, Lewis structures remain a very useful aid in describing the bonding in a molecule, and for quickly determining its approximate structure and geometry.

The Octet Rule

The rule of eight proposed by Lewis, but renamed the octet rule by Langmuir, is a much less useful rule than the rule of two because it is often not obeyed by the elements of periods 3 and beyond, as was recognized by Lewis, but not so clearly by Langmuir who popularized the rule. Consequently, the octet rule came to play a much more important role in discussions of bonding than was justified and led to the unnecessary concepts of hypervalence and hypovalence. Today it cannot be regarded as a universal rule except for the period 2 elements C, N, O, and F, although it still has some usefulness for introductory chemistry courses, provided its limitations can subsequently made clear.

Electrons are Not Always in Well-Localized Pairs

Electron pairs are of course not localized in Lewis's original sense. They only have a most probable distribution. However, they are often most probably to be found in a single bonding or nonbonding domain and are localized in that sense. However, in many molecules the electron pairs are not so localized but they can still be satisfactorily described by Lewis structures used as resonance structures, as demonstrated by Pauling. But the description of molecules in terms of resonance structures using localized pairs becomes increasingly difficult with increasing delocalization of the electrons and the need to use a large number of resonance structures to describe the bonding, at which point the MO theory becomes more satisfactory. Opposite spin electrons only form localized pairs when there is a sufficient force to draw them together against their electrostatic repulsion. In linear molecules, only the electrons along the molecular axis are paired. The six nonbonding electrons in the valence shell of a monatomic ligand are not paired. Linnett's double quartet theory provides an explanation as to why electrons in molecules are not always paired and provides a method of representing the electronic structures of such molecules.

The Chemical Bond

Although Lewis stated that he took the shared electron pair to be the chemical bond, the chemical bond is not a real measurable object and it cannot be clearly defined. Lewis did not in fact define a chemical bond but he did propose a very useful model although the real meaning of "sharing" was not really clear for many years. Today, we understand a shared pair to be a pair of opposite spin electrons that has a high probability of being located between two atoms that are strongly bound together. The chemical bond remains a very useful, but qualitative, concept that cannot be clearly defined, just like other qualitative concepts such as electronegativity and bond polarity that have proved to be very useful during the development of chemistry. They should not be dismissed because they are only qualitative concepts unlike the quantitative laws of physics. Chemistry became a well recognized and practically useful discipline almost independently of the development of physics. Nevertheless, it has sometimes been said that chemistry is just a branch of physics implying that all of chemistry could be derived from the fundamental laws of physics. Perhaps, far in the future, this might be the case, but in the meantime we should be grateful to pioneers such as Lewis who introduced valuable concepts long before they could have been deduced from the laws of physics. In short, chemistry is not physics, although as they develop they become intertwined and occasionally merge with each other.

Lewis's Other Contributions to Chemistry

In conclusion, it should not be forgotten that in addition to Lewis's enormous contribution to our understanding of chemical bonding, he made several other important and lasting contributions to chemistry, including in particular his pioneering work on thermodynamics, and his work on acid–base theory. He was one of the truly great figures in the history and development of chemistry.

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