

Essay

The Lewis Legacy: The Chemical Bond—A Territory and Heartland of Chemistry

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Abstract: Is chemistry a science without a territory? I argue that “chemical bonding” has been a traditional chemical territory ever since the chemical community amalgamated in the seventeenth century, and even before. The modern charter of this territory is Gilbert Newton Lewis, who started the “*electronic structure revolution in chemistry*.” As a tribute to Lewis, I describe here three of his key papers from the years 1913, 1916, and 1923, and analyze them. Lewis has defined the quantum unit, the “electron pair bond,” for construction of a chemical universe, and in so doing he charted a vast chemical territory and affected most profoundly the mental map of chemistry for generations ahead. Nevertheless, not all is known about the chemical bond” the chemical territory is still teeming with new and exciting problems of in new materials, nanoparticles, quantum dots, metalloenzymes, bonding at surface-vapor interfaces, and so on and so forth.

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Introduction

The historians Bensaude-Vincent and Stengers¹ define the image of chemistry as a science without a territory, or a science with a dismembered territory, the *Jean sans Terre* of Sciences. Indeed, many scientists, even chemists, share a feeling that chemistry while being a central science had moved afar from its center to merge within other sciences and to fructify them; it has become an invaluable servant.¹ And while exhibiting exciting activity, knowing no bounds, still chemistry has been losing gradually its identity, its territory of fundamental questions. There are even some thoughts, debated recently in the chemical magazine *C&E News*, to change the name of the Science and eliminate the term chemistry altogether.²

One of the fundamental territories of chemistry is the chemical bond, the element from which an entire chemical universe is constructed. This chemical theory serves as a bridge between the apparent magic of chemistry (the chemical transmutation) and the way this magic is represented to day in terms of molecules changing into one another. Nevertheless, the current activity of the chemical community in discovering fundamental bonding issues, new bonding features, etc, is not overwhelmingly intense. Chemists have in fact, by and large, abandoned their territory as if everything about bonding is known and well understood; the

frontier has moved to Nano and Bio, leaving the original territory untended.

Before proceeding, let me attempt to establish a claim on the chemical bond as a territory of chemistry, because with the advent of quantum mechanics, there is a tendency to annex this territory to physics. Since I am not a historian, and would like to avoid “playing tricks on the dead,” as Siegfried musingly defines the task of the historian,³ I will simply bring my personal impressions on the matter as shaped by necessarily selective reading.

The idea of “bonding” may even have alchemical origins in the spiritual outlook of matter, where the *conjunctio* or union of the opposites is the ultimate synthesis necessary to drive the change of lower matter to gold.⁴ In chemistry, the roots of the bond concept date way back to the efforts of chemists to grapple with the magic of chemistry, the formation substances and their transmutation;³ these efforts led to the formulation of “chemical theories” where “affinities” were considered to unite substances. It is important to note that, as is the usual case in chemistry, the bond was not defined as a static property of substances but as a dynamic one, in conformity with the “chemical magic” that a substance exists one time and then disappears making place for a new one.

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In 1675, Lemery published his book “*Course de Chymie*”⁵ (see also ref. 3, pp. 76, 79, 83, 93–96) and used “elective affinities” as terminology that describes the replacement of one metal by others in the chemistry of salts (see ref. 3, pp. 79, 83, 94). In 1718 (a year after the second edition of Newton’s “*Opticks*”), Etienne Francois Geoffroy systematized this phenomenon in his table of “*rappports*” (see ref. 3, pp. 76, 93–96). The historian Ursula Klein⁶ credits Geoffroy as the first to generalize the basic concept of modern chemistry—that of the “compound” with “chemical affinity” between the constituents. Building on Geoffroy’s “theory,” another Frenchman, Peirre-Joseph Macquer published in 1749–1751 his two volume monographs: “*Chimie Theorique*” and “*Chimie Pratique*,”⁷ in which he gave rules of chemical combination. As cited by the Historian Siegfried, these rules sound very modern to our contemporary ear (see ref. 3, p. 144). For example: (a) if one substance has any affinity or rapport (conformity) with another, the two will unite together and form one compound; (b) Substances that unite together lose some of the separate properties; (c) The simpler the substance, the stronger its affinity. In 1744, another French chemist, Guillaume Francois Rouelle, differentiated the sciences of chemistry and physics referring to the “force” that combine chemical elements (see ref. 3, pp. 134–138): “The mechanical philosophy now provided a new justification for the philosophical inability to isolate the elements. Bodies combined with one another because of some kind of attractive force.” The notion of “elective affinity” reappears some 70 years after the publication of Geoffroy’s table of “*rappports*,” in the colossal work of Swedish chemist Torben Bergman who assembled thousands of reactions into elective attraction/affinity tables (see ref. 1, pp. 69, 70). The elective affinity in Torben’s tables was a “go-no go” situation, and reflected in essence the selective combination that marks chemistry and is very different than the “physical forces” of mixing or mechanical forces between bodies.

However, a significant change had to occur to put the “elective affinity” into the effective theoretical construct, we now call “the chemical bond.” This change was induced by two consecutive revolutions. The first revolution is the “compositional revolution” that started with Lavoisier and culminated in the atomic hypothesis of Dalton, which enabled him to identify the abstract almost mythical term “elementary bodies” with discrete atoms; matter with “quantized weights” (see ref. 3, p. 237). This hypothesis has developed into quantitative compositional rules that have led eventually to the notion of the molecule with the work of Cannizzaro, who demonstrated the importance of Avogadro’s hypothesis (see ref. 3, pp. 260–262). Now, the chemical community had in its possession the elements that could bond, and bonding theories started to form gradually and replace the “affinities.” There were the “dualistic” electrical theories of Davy and Berzelius⁸ (see ref. 1, p. 75), which sprung from electrochemistry. A similar theory was delineated later by Thomson, the discoverer of the electron, in which bonding arose from attraction of oppositely charge ions after electron transfer between the atoms.^{8,9} Later, this theory was replaced by a more advance theory¹⁰ where bonds were formed by Faraday “tubes” (lines of force) from one atom to another and vice versa. This has created a vogue of ionic or the so-called ‘electromer’ theory, especially amongst American scientists.⁹ However, from their

onset, these “ionic” type theories have been disreputed by the concept of “valence” that sprung from organic chemistry, and from dealing with nonpolar (nonionic) substances, and that united the structuralists, Kekule, Couper, Butlerov, and so on. This dichotomy and the urge to generalize chemistry and create an Allgemeine Chemie (a unified chemistry),^{11,12} has eventually led to the second revolution, “the electronic structure revolution,” culminated in the Lewis hypothesis of the electron pair bond in 1916, which gave the clue to the nature of the atomic combination.¹³ At last, the meaning of the mythical terms “elective affinity” and “elective forces” had an operational and an effective definition that allowed to construct a chemical universe. This was followed by reformulation of the Lewis ideas by the emerging quantum mechanical theory, first by Heitler and London,¹⁴ and subsequently by Pauling,¹⁵ Slater,¹⁶ and so on. Indeed, like in a religion, the new temple would be built upon the mythical shrines of the old religion. Thus, although the final dress of the chemical bond has a physics’ touch, with the exception of Thomson, who was avidly interested in chemistry,⁹ physicists were relatively late comers to theorize an effective chemical bonding mechanism. In this sense, it is noteworthy to find that in 1923, good 7 years after Lewis’ publication, Born writes to Einstein about his perplexing attempts to understand the “homeoplar bonding forces” as those holding H₂, and adds: “Unfortunately, every attempt to clarify the concept fails.”¹⁷ Yes, Lewis did not try to understand the “forces”; instead, he let himself be guided by his chemical overview to hypothesize the pairing as a quantized unit of bonding, which gave the clue to the nature of the atomic combination.¹⁸

From Lewis to Pauling: A Story in Brief

The concept of the electron pair bond was formulated in a stroke of genius by Lewis (Fig. 1) in his famous 1916 JACS article, “The Atom and the Molecule.”¹³ Lewis was seeking an understanding of the behavior of strong and weak electrolytes in solution (see ref. 11, p. 135). And like the Biblical King, Saul, who went seeking for his father’s asses and found a kingdom, so did Lewis find the concept of the electron pair bond as an intrinsic property that stretches between the covalent and ionic situations. This work has eventually had its greatest impact in chemistry through the work of Irving Langmuir,¹⁹ who very ably articulated the Lewis concept, coining new and catchy terms.²⁰ Another important influence of the Lewis ideas was on the understanding of reaction mechanisms as established by the English School of Lapworth, Robinson, Lowry, and Ingold.^{17,18} This has eventually led to the development of the science of physical organic chemistry,²¹ which rules mechanistic thinking even today (even though the science itself as an active discipline is no more with us . . .).

The overwhelming chemical evidence that supported the Lewis model presented an exciting agenda for research directed toward understanding the mechanism whereby the electron pair could constitute a bond. This, however, remained mysterious until 1927, when Walter Heitler and Fritz London went to Zürich to work with Schrödinger. In the summer of the same year, they published their seminal papers,^{14,22} which showed that the



Figure 1. A caricature of Lewis, graciously provided by W.B. Jensen.

bond energy in H_2 is due to the resonance between the electrons as they exchange positions between the two atoms. In the winter of 1928, London²² drew the basic principles of the nonionic bond, and his theory was in essence a quantum mechanical articulation of Lewis' covalent bond. Lewis is not cited in these papers; this omission may simply reflect the rift that exists between the two communities. Nevertheless, a chemist who was a resident in the two communities was Pauling, and he writes to Lewis²³ in 1928 about the exciting verification of his ideas by Heitler and London. The work of Heitler and London has culminated in the colossal intellectual construct of Pauling, who described the electron pair bond as a superposition of covalent and ionic forms, and thereby enabled the description of any bond in any molecules. In Pauling's work, the long sought for *Allgemeine Chemie* of Ostwald, the father of physical chemistry, was finally achieved. Nevertheless, reading Lewis' paper shows that he anticipated the ideas that underlied the physical organic school^{18,20,23} of Ingold and the resonance concept^{18,24} expounded by Pauling. Indeed, Pauling himself dedicated his monograph²⁵ to Lewis, thereby expressing the link and influence of Lewis' work on his. As noted by Hager,²⁶ Pauling's biographer, Pauling discovered Lewis' 1916 paper¹³ by reading Langmuir's¹⁹ 1919 paper. Until reading these two papers in 1920, Pauling had been teaching a chemistry course at Oregon Agricultural College in which he used the image of a chemical bond as one of hooks and eyes, e.g., with the sodium atom having an eye and chlorine having a hook.

Three of Lewis' Papers 1913–1923

Since this volume is dedicated to the 90th year of the Lewis concept of electron pair bonding, I deemed it appropriate to pay

tribute to Lewis, and describe three key papers, which summarize his thought. The first paper is a 1913 JACS article,²⁷ which preceded the historical 1916 paper,¹³ and finally his short presentation in the 1923 Faraday Society Discussion.²⁸ I shall analyze the three papers, and will point out the lineage they form to many of the concepts that dominate our chemical thought.

Before proceeding, let me just remark that reading these papers of Lewis are almost like hearing him speak to you. The style is personal, vivid, and engaging, and the breadth of the intellect is dazzling. Once in a while, the style would become sociably tactful, like when the author gives credit to others, or wishing to establish his own priority. Other times there would be a note indicating broad understanding of the social forces of science, for example¹³ when he talks about the rivalry between the "dualistic" and the "valence" theories, he writes "there has always been that antagonism between the two views, which invariably results when two rival theories are mutually exclusive, while both contain certain elements of truth." During reading, I felt sorry that we do not write anymore like that, or are inhibited doing so.

1913: The Covalent–Ionic–Metallic Bonding Classification

The first paper "Valence and Tautomerism"²⁷ appears back to back with the paper of Bray (his colleague) and Branch (Lewis's PhD student²⁰).²⁹ Lewis opens by thanking Bray and Branch, for helping to clear the haze created by the term "valence" through their definition of "valence numbers" and "polar numbers." He redefines these numbers: "the valence number is the number of bond termini at the atom, at which attachment to corresponding points on other atoms occurs; the polar number is the number of negative electrons, which an atom has lost (in algebraic sense)." Thus, he makes the distinction used today between the number of bonds (coordination number) and the "oxidation state" of the atom. With this preamble, Lewis proceeds to the key point of the paper:

"Apparently, we must recognize the existence of two types of chemical combination, which differ, not merely in degree but in kind. To illustrate the two types, we may choose a salt-like potassium chloride, and a paraffin hydrocarbon such as methane. The first type may be called polar, the second nonpolar."

Thus, Lewis looks at chemistry coming out from two branches separated by rift, inorganic chemistry and organic chemistry, and unifies them in terms of bonding types, which he still calls "chemical combinations," and which are the ionic and covalent bonds in today's language. In the end of the article, he adds a third bond-type, the metallic:

"In the first type, the electrons occupy fixed positions within the atom. In the second type, the electrons move freely from atom to atom within the molecule. In the third or metallic type, the electron is free to move even outside of the molecule."

This is probably the first such distinction made by a chemist and it precedes a similar ionic–nonionic distinction made by Thomson, one year later.¹⁰

On the basis of this classification, Lewis then characterizes the properties endowed by these bonds on chemical substances; his principles are clearly electronic (he refers to the electron as "the atom of electricity") as well as structural ones. According

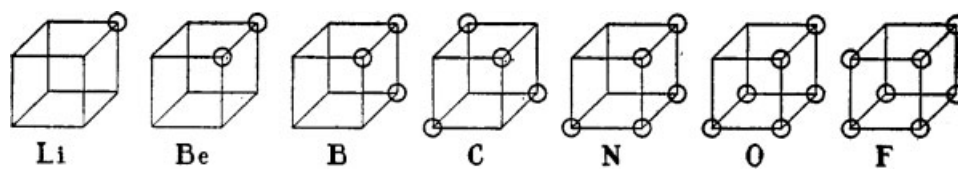


Figure 2. The cubical atom. Reproduced from ref. 13 with permission of the ACS.

to this characterization, to the organic or nonpolar compounds “we may ascribe a ... fixed arrangement of the atoms within the molecules, which permits us to describe accurately the physical and chemical properties of a substance by a single structure formula.” As such, “valence numbers” of atoms must be integers. On the other hand, “in the polar compounds free charges exist at certain points of space,” and this explains the “tendency of these substances to form ions ...” And although ionic substances have structures, “the atoms must be regarded as moving freely from one position to another, falling now into one places, now into another, like the bits of glass in a kaleidoscope.” Furthermore, “since the prime consideration is the distribution of electrons in the molecule,” one can use “polar numbers” (oxidation states) to characterize the atoms. Lewis uses two terms that are very familiar to us; the dynamic structure is called by him “tautomerism,” and the name “electrophile” is used by him to describe the tendency of polar substances to form electrolytes. The latter term was coined by Lewis and Wheeler in 1909 and will be resurrected by Ingold to describe a reactivity feature of “electron poor” molecules.

Despite this clear-cut classification, Lewis recognizes very well that the two extreme classes are idealized and that there are plenty of organic substances that possess, in the same molecule, polar-regions in addition to nonpolar ones. He discusses experimental evidence of polarity of organic substances, and of the tendency of organic molecules as well as nonpolar molecules to assume polar forms, such as the dissociation of acetic acid, the conductance of liquid I_2 , and so on. It is clear already here that Lewis is thinking about a “polar–nonpolar” superposition, which will become a cornerstone in Pauling’s theory of bonding. The same applies to the metallic bond, where alloys (e.g., $NaPb_2$) show both “metallic” and ionic behaviors under different conditions. Here, Lewis speaks about electronic tautomerism (“tautomerism between polar and no-polar ...”), which may be thought of as the precursor of “resonance theory” employed by Pauling as a centerpiece of his intellectual construct.^{18,24}

The finale of the paper is typical of Lewis’ self-assured style: “All known chemical compounds may be grouped in the three classes: nonpolar, polar, and metallic; except in so far as the same compound may in part or at times fall under two of these groups.”

1916: The Octet Rule, the Duet Rule, and the Electron Pair Bond

Three years after the 1913 paper, Lewis publishes his second and most important paper about bonding, which he called “The Atom and the Molecule,”¹³ a very fitting title to follow the compositional revolution of Dalton with yet another one, the electronic structure revolution. The paper is hierarchical and has a

tempo that accelerates as the pages progress. The concepts are built gradually, initially slowly, with digressions along the way, and then with increased pace toward a converging finale. The increased pace intensifies the impression of a sense of discovery that must have driven Lewis during the act of writing itself.

In the opening of the paper, Lewis establishes priority on the territory. He first reminds his readers that he has already classified the atomic combination types in his 1913 paper. He also cites the 1914 Thomson’s paper¹⁰ that gave a similar classification unknowingly of Lewis’ 1913 paper.²⁷ He accordingly writes: “This article [Lewis’ 1913 paper] was apparently unknown to Sir J.J. Thomson when he wrote, in 1914, an extremely interesting paper on the ‘Forces between Atoms and Chemical Affinity’ in which he reached conclusions in striking accord with mine.” Lewis then reiterates his polar–nonpolar classification, and asserts that this classification could have been based solely on chemical knowledge, but that it would be better to derive it from some theory of atomic structure. At this point, he moves to establish a second priority, now over his cubical atomic theory and does so twice: He first writes on page 763, “Such a theory I have employed for years ... but it has not hitherto been published.” He will do so again on page 767 when he introduces this theory, ‘The Cubical Atom,’ in a pictorial manner (Fig. 2 in his paper, and Fig. 2 here), he writes “A number of years ago, to account for the striking fact ... I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to my colleagues, has never been published ...,” and he adds a footnote: “These figures are taken from a memorandum dated March 28, 1902 ...,” and then he explains his reasons for exacting this date: “The date of origin of this theory is mentioned ... because the fact that similar theories have been developed independently adds to the probability that all possess some characteristics of fundamental reality.” What an interesting way of reasoning your priority and the validity of your theory! As a side remark, one can find in the website of “The Chemical Heritage Foundation” the Lewis’s memorandum of 1902, showing his cartoon representation of the cubical atom, which appears also on page 29 of his classic monograph.³⁰

Following this introduction, Lewis reminds the reader of the properties that mark polar and nonpolar substances, more clearly than he did in 1913. He defines polar molecules in which “one or more electrons are held by sufficiently weak constraints so that they become separated from their former positions in the atom ... thus produce a bipole or multipole of high electrical moment;” this is an ionic bond and as a prototype Lewis cites sodium chloride. Then he defines the nonpolar molecule “as one in which the electron belonging to the individual atom are held ... [and] do not move far from their normal positions ...” It is clear from the subsequent text that he does not view these properties as static ones; nonpolar molecules can acquire polar

characters in the presence of other polar substances or in a polar environment. He makes clear that he believes that the variation is gradual, and writes: "... but scanning the whole field of chemical phenomena, I believe ... that the distinction between the most extreme polar and nonpolar types is only one of a degree, and that a single molecule ... may pass from one extreme type to another, not by a sudden and discontinuous change, but by imperceptible gradation." It is apparent therefore that his view of the bond is as a dynamic entity that can change its character, e.g., by a reaction in a medium, and that the covalent-ionic property is in his view a continuous scale and not an either/or classification. The strength of his ideas derives from the foundation based on his vast chemical knowledge. These ideas will reappear in modern dresses in the physical organic chemistry school and in the Pauling theory of the chemical bond.

The Cubical Atom and the Octet Rule

Lewis mentions that his theory was born in an attempt to accounts for Abegg's law of valence and countervalence,²⁰ namely that the total difference between the valence and oxidation state numbers "is often eight and in no case more than eight." This is the first time, he mentions in the paper the term that will be known later¹⁹ as the "octet rule" (a similar rule was published at the same time by Kossel²⁰ and the roots of the "eight" rule date back to Mendeleev.²⁰) His cubical atomic picture is reproduced here in Figure 2, where the "circles represent the electrons in the outer shell of the neutral atom." Clearly, there were other electronic models of the atom (Thomson, Bohr, Kossel,²⁰ etc) in 1916, but the choice of a cube made by Lewis is a clever one because its three-dimensionality provides an immediate entrance to three-dimensional structures.

On the basis of the cubical model, Lewis starts with a few fundamental hypotheses:

- a. The first three hypotheses (1–3) refer to the separation of the atom into "kernel" and "outer shell" (suggested before by Thomson²⁰), which in modern use is a "core-valence" separation, and the rule of eight, later to be called¹⁹ the Octet Rule. The valence shell, according to Lewis, contains "negative electrons equal in number to the excess positive charges of the [core]." The number of electrons in the valence shell can change during a chemical reaction between the limits 0–8. Thus, "The atoms tend to hold an even number of electrons in the shell [valence shell], and especially to hold eight electrons, which are normally arranged symmetrically at the eight corners of the cube." In these postulates, Lewis makes an effective dissection of the atom, focuses on the important part the valence shell, and establishes the octet rule as an upper bound for electronic changes.
- b. The chemical bond postulates (4–6): Lewis starts by stating that the atomic shells are "mutually penetratable," namely, he defines thereby the act of bonding. He then proceeds to say that while electrons may exchange positions in the valence shell, nevertheless, they are held in position by rigid constraints that are determined by the nature of the atom and of the "other atoms that are combined with it." Finally, he asserts that electrical forces "between particles which are

very close together do not obey the simple law of inverse squares [Coulomb's law] which hold at greater distances."

The chemical bond will be clearly defined only later in the article, but already here we can see the amount of insight: First, chemical bonding obeys magic numbers (octet), it is not a merely quantitative property of size like attraction between massive bodies. We then see seminal notions of overlap, time-independence of the molecular electron density, and the molecular stereochemistry fixed by electrons. Not that Lewis could have really written "overlap" or "time independence of electron density," as we define these terms today, but the notion of interpenetrability of the shells and the fixation of electrons in space have already the nuclear myths for establishing later the bonding theory, the new religion. And a final remark concerns Lewis's personality as suggested by his 6th postulate; he is not afraid to abandon a useful law when faced with a situation that demands it. This is the type of courage that was displayed for example by Niels Bohr a few years earlier, the courage of reformers.

Having these postulates, Lewis proceeds to construct a chemical world in stages, and he does so in a didactic manner that can appeal to the fellow chemists, albeit may not impress fellow physicists. In the first stage, he starts by considering atoms relative to the "stable" Neon, i.e., their "distance" from the octet. Then he continues with a valence shell electron count in a variety of molecules showing how the total number of electrons comes in multiples of the magic number 8. In doing so, he makes another important observation-turned-into-a-rule, namely that all stable species have an even number of electrons. To reinforce the even rule, he discusses some odd electron species, like the trityl radical, $\text{Ph}_3\text{C}\cdot$ or nitrogen dioxide, $\text{NO}_2\cdot$, and notes that in solution or condensed phases, these species will generally give up an electron or gain one, e.g., "in a polar medium, the odd electron may be given up completely."

The Octet and Duet Rules

In the next stage of his construction of a chemical world, Lewis turns to the key question, the nature of the chemical bond. As he usually does, he starts with an introduction of what preceded him, and writes: "Ever since the first suggestion of Helmholtz [1881], numerous efforts have been made to explain chemical combination by the assumption that in the formation of a compound some of the electrons of one atom pass completely into another atom, and that the different charged parts of the molecule thus produced are held together by electrical forces." There is clearly a tension here and Lewis feels he has to clear the way for his approach. He will later reconcile the two different approaches.³¹ His opinion on the "ionic" theory is succinctly stated: "Such theories have, in my opinion, proved entirely inadequate except in the case of substances of strongly polar type." He then adds that this inadequacy has been recognized by Thomson who treated, in 1914, the bonds between in nonpolar combination in a different way¹⁰ (as we recall, Thomson suggested that atoms bind when their electrons apply mutually lines of force (tubes of force) that start from the atom of origins and terminate at the bonded atom, and vice versa). Lewis states that invoking two kinds of bonds is not really necessary, but only in

the extreme case, since polar and nonpolar compounds differ in degree and not in kind. Now the way is cleared to mention the origins of his bond concept by applying his fourth hypothesis, the interpenetrability of electronic charges of two atoms. He writes: "Thus an electron may form a part of the shells [valence shells] of two different atoms and cannot be said to belong to either exclusively. Hence in general, it is impossible to say that one element in a compound has been oxidized or reduced. . . but it is only as we approach the substances of completely polar type that such distinctions become less and less ambiguous." Most living chemists will agree with him. . .

However, the way is still not completely clear, because the forces of bonding are not yet defined. Lewis then has to continue to consider existing theories to inquire if they include a suitable mechanism. His conclusion is negative. He mentions the theory of Bohr and defines it as being logically objectionable, "for the state of motion that produces no physical effect whatsoever may better be called a state of rest." He then concludes that it is futile to use the existing electromagnetic theory and builds up a mechanical model of the atom based on an attraction between the positive and negative constituents of the atom. His conclusion that in such a case as in the atom, chemical reasoning and the mathematical theory of the electrons leads to the conclusion that "Coulombs law . . . must fail at short distances." As such, he suggests, the law has to be abandoned in the case of the atom, and that this would not be the first time that "an increase in the range of observational material has acquired a modification of generalizations based upon a smaller field of observation." Lewis then considers Parson's magneton's theory (published in 1915), which assumes that electrons apply also magnetic forces on each other. He finds a lot to like about this theory, which leads also to the conclusion about the group of eight electrons arranged in the corner of a cube. But he mentions that new measurements by Moseley show "that helium has a total not of eight but of either four or two electrons," and that "from the resemblance of this element to the other inert gases," one may conclude that "here [Helium] the pair of electrons plays the same role as the group of eight in the heavier elements, and that in the row of . . . comprising hydrogen and helium we have in place of the rule of eight the rule of two." Here, Lewis recognizes that in addition to the octet rule, hydrogen, helium, and lithium obey the "duet rule," and immediately classifies, LiF, LiCl, and LiH as salts in which the Li and H attained duet and reached configurational stability.

Molecular Structure

Now Lewis proceeds with his grand construction scheme. He starts with a self-assured statement: "I shall now attempt to show how, by a single type of chemical combination, we may explain the widely varying phenomenon of chemical change." His preliminary pictures are still odd looking to the modern eye because they are based on the cube, but not for long. He starts his discussion different putative states of a dihalogen like I_2 , according to Figure 3.

In A, he shows a situation of complete ionization (to I^- and I^+ ?) "as is undoubtedly is to a measurable extent in liquid iodine," which conducts electricity. Without ionization one atom

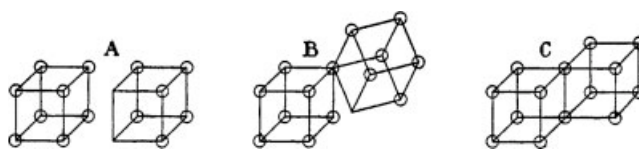


Figure 3. Three states of a bond. Reproduced from ref. 13 with permission of the ACS.

can complete its group of eight when "one of the electrons of one atom fitting into the outer shell of the second atom," as in B. And finally, in C, he argues that "at the same time an electron of the second atom may fit into the shell of the first, thus satisfying both groups of eight and giving the form C which is the predominant and characteristic structure of the halogens." Thus, structure C involves an electron pair bonding and the "shared bond" (the common edge of the two cubes in C) later to be called¹⁹ the covalent bond.

Lewis then goes through a long discussion of the behavior of form C in polar media and the differences between the different halogens. Here he expresses a few "futuristic" ideas and the number of ideas within one page is truly dizzying (p 775, 776). One is that form C is not static but may involve situations where the two electrons may cling sometimes to one of the atoms, sometimes to the other. This idea in a modern dress is Pauling's covalent-ionic superposition of the electron pair bond. Within this idea, Lewis discusses the notion of tautomerism as electronic phenomenon: "But we must assume. . . that these forms represent two limiting types, and that the individual molecules range all the way from one limit to the other"; this idea is reiterated near the end of the article when Lewis uses it to discuss the color of compounds because of the oscillation of "loose" electrons between extreme situations in the molecule. In an altered dress, the idea will become the mesomerism theory of Ingold.¹⁸ In the same discussion, Lewis considers intermediate cases in between the extremes—this is a seminal notion of the resonance theory.²⁴ Lewis further uses this mechanism of the dynamic position of the two electrons to discuss heterolysis in solution, when an electron pair moves to one of the atoms. This idea will flesh out in the curved arrow used by Robinson to describe reaction mechanism, and later by Ingold and Huges to describe heterolytic processes in organic molecules. Of course, there is no claim here that the ideas have been taken from Lewis and dressed differently. The point is that past notions are learnt and assimilated, and in the face of a new set of problems, the concepts resurface in minds different than the originator's and necessarily so in different dresses that fit the problems and the times.

The Finale—Bond Symbols and the Emergence of the Electron Pair as the Fundamental Quantum of Bonding

Following this discussion and speculative digressions, Lewis starts (p 776) with the finale. The new idea, like any religion, requires a new symbol, and Lewis writes: "In order to express this idea of chemical union in symbols I would suggest the use of a colon. . . to represent the two electrons which act as the connecting links between the two atoms. Thus we may write Cl_2



Figure 4. Two forms representing the behavior of the double bond in ethylene.

as Cl:Cl . . .” (see Fig. 1). With a single pictogram, Lewis uses the Berzelius’ language of representing molecules (e.g., H₂O) and the structural diagrams of the structuralists, to which he adds the notion of the electron-pair bond; what an ingeniously portable device! He uses this symbol further to depict the H₂ molecule as H:H and the somewhat polar molecule HCl as H:Cl, where the electron pair is displaced toward Cl. Using the octet rule and the colon symbol, he solves the constitution of ammonium as a species with four N:H bonds (previously, it was represented as ammonia complexed to H⁺). The perchlorate ion is drawn in a very modern way (no extension of octet is allowed, as every theoretician will tell you that . . .), with four Cl:O bonds and all atoms obeying the octet and having formal charges.

Next, Lewis proceeds to consider a double bond, “in which four electrons are held conjointly by the atoms.” Since he recalls the tendency of the double bond to break, he presents the double bond in two “tautomeric forms” (discarding a third one with an ionic distribution). Figure 4 shows his representation of the ethylene molecule, as a tautomeric blend of two structures, one with a double bond and one a diradical. The O₂ molecule is represented in the same manner, where the doubly bonded structure corresponds to the low temperature form and the diradical is the high temperature form.

Lewis makes another conceptual leap, when he reaches the triple bond, and states that it cannot be represented using the cubical atom model. He then reminds the readers of the molecules that obey the duet rule and writes: “and we may question whether in general the pair rather than the group of eight should not be regarded as the fundamental unit.” He explains that the cubical atom obeys the principle of least repulsion between the electrons, but in small atoms the pairs may tend to be drawn together by some short range forces, and form another configuration of four electron pairs organized symmetrically around the center of the cube in a tetrahedral arrangement. Thus, in one sweep, Lewis introduces the idea of the tetrahedral carbon into the electronic structure—clearly, a modern element of structural chemistry, and a seminal VSEPR idea. With such a model one can describe all bonds types: “two tetrahedra attached by one, two, or three corners of each, represent respectively the single, double, and the triple bond. Lewis then proceeds to generalize and discusses rings, strain, etc. He considers conjugated molecules, and recognizes the “mobility” of these electrons, and hence the reactivity of the conjugated parts of the system derives from the freedom of the electrons to rearrange—here again, is the seminal idea of the curved arrow. Finally, Lewis summarizes his views on organic molecules in a succinct statement that:

“[M]olecules are held together by the pairs of electrons which are held jointly by the component atoms.”

In the final part of the paper, Lewis attempt to reconcile between the two great traditions of chemistry, the electrochemical theory of Berzelius and Davy, and the valence theory of the

organic chemists. He argues that his model unifies the two schools, “for the ‘valence’ theory, which is the classical basis of structural organic chemistry, deals with the fundamental structure of the molecule, while the electrochemical considerations show the influence of positive and negative groups in minor distortions of the fundamental form.” He then proceeds to define what we would call today electronegativity, using the electron pair bonding. Thus a negative element “draws toward itself the electron pairs, which constitute the outer shells of all neighboring atoms, and the electropositive group is one that attracts to a lesser extent or repels these electrons.” He then discusses the polarity of bonds in molecules, methane with a slightly negative carbon and slightly positive hydrogen atom, while CCl₄ with slightly positive carbon and negative chlorines. He proceeds to show how the electronegative chlorine in e.g., ClCH₂CO₂H enhances its acidity relative to CH₃CO₂H by withdrawing electrons and this electron withdrawal is transmitted to the hydroxyl group of the acid and cause “a greater separation of the electrons from the hydrogen . . . and thus a stronger acid.” He talks about the variation in the effect: “The effect is less marked the greater the distance . . .” This is clearly the “inductive effect” that has been employed later in Ingold’s theory of physical organic chemistry alongside mesomerism and tautomerism. Any new religion has always more ancient foundations.

After completing this tour de force, Lewis is ready to rest his case. For me, the true finale of his paper is on page 782:

“This brief account . . . could be extended almost indefinitely . . . but I believe enough has been said to show how, through simple hypotheses, we may explain the most diverse types of chemical union and how we may construct models which illustrate the continuous transition between the most polar and the most nonpolar of substances.” A real climax!

Before proceeding to the third paper, it is fair to point out that a model of shared electron pair bonding was proposed as early as 1908 by Johannes Stark and Hugo Kauffmann. But as explained by Jensen,³² they failed to extend their model and to apply it to larger molecules, in the effective manner that was done by Lewis.

1923: The Prophet of Chemical Bonding—A Mature Summary of the Key Ideas

In 1923, the Royal Society organized the Faraday Discussion Meeting on “The Electronic Theory of Valence.” A Faraday Discussion Meeting is a spectacular event that is run like a play with the key actors in the field. Sir J.J. Thomson is the Chairman of this meeting and Lewis is the Keynote Lecturer. Among the speakers/participants are stars of the English school: Sir William Bragg, Thomas M. Lowry, Sir Robert Robinson, Arthur Lapworth, Neville Sidgwick, as well as famous American scientists like William A. Noyes, the JACS editor and an author of a bonding theory himself,⁸ and a quite a few other scientists. The Chairman opens with a short speech about the electron in chemistry and states: “The electron dominates the field of chemistry.” Then he invites Lewis to deliver his address²⁸ to the discussion.

By that time, Lewis’s book is in the galley proof stage, and his fame is worldwide; this is a time to summarize, give princi-

ples, and smoothen frictions. Lewis opens with his goals “to secure agreement between conflicting opinions.” He starts by building bridges to rival or dissenting views coming from physics. His first comment concerns the apparent contradiction between atomic models of the physicists (Bohr’s model) and the chemists (Lewis’s model); “the facts of chemistry . . . require a static atom . . .,” while the facts of spectroscopy and magnetism indicate “the presence of rapidly moving electrons within the atom.” This difference is reconciled brilliantly: when Lewis speaks of the “location of an electron” as in his cubical atom or tetrahedral arrangement of the electron pairs about carbon, he means the “position of [Bohr’s] orbit as a whole” in space, which is of course fixed. Building this bridge, he then proceeds to talk about the principles of his own theory, emphasizing the electron pairing and the single most important mechanism of chemical bonding.

The Importance of Electron Pairing

Lewis starts with the Bohr theory of electron shells, and notes the “predominance of this group of eight electrons in valence shells,” so much so that the new theory of valence has been called the “octet theory” (here he alludes to the terminology Langmuir¹⁹ used for the Rule of eight of Lewis and Kossel). And although Lewis himself once emphasized the rule, we in fact witnessed above that already in 1916 he went beyond this rule and concluded that, “The cardinal phenomenon of all chemistry is the formation of the electron pair.” This new conclusion, he says, was based on his recognition that the great majority of some hundred thousand known substances have an even number of electrons. He then adds a very strong statement: “The universality of this pairing of electrons points definitely to an actual physical coupling of the electronic orbits. When two molecules, each of which possess an odd electron, combine with one another, it is as though the unpaired electrons were clamped together by some powerful mechanism.” He brings forth evidence for this pairing from the fact that molecules with an even number of electrons do not have magnetic moments (he notes very few exceptions, probably O_2 ?), whereas all species with an uneven number of electrons have magnetic moments. Thus he says: “from our magnetic data alone we should conclude that two electronic orbits, each of which acts as a magnet, normally conjugate with one another to form a system without magnetic moment.” He is well aware that the neutralization of the electronic magnetism through coupling is not a classical magnetic force, and that currently quantum theory has no such mechanism, and concludes that: “For the present it will be sufficient to assert that the coupling of two electric orbits, with the neutralization of the magnetic fields, is the most fundamental of chemical phenomena.” Moreover, he asserts that “these pairs are symmetrically arranged about the atom,” as for example in carbon “four such pairs are situated at the corners of a regular tetrahedron, forming the normal octet.” One can clearly see here the seeds of the later quantum-based hybridization theory and the much latter developed VSEPR approach to chemical structure.³³

Now, that the importance of pairing is established Lewis makes one more step and defines the elements of electronic structure in molecules:

The Electron Pair as the Chemical Bond

First Lewis equates the pair with a bond, and says: “When the electron pair is situated between two atoms and thus may be said to belong jointly to the two atoms, it is the agent of chemical union. Whether we are dealing with organic or inorganic compounds, the chemical bond is always such a pair of electrons.”

The Lone Pair—An Element of Electronic Structure

A further articulation of the electron pairing idea is the introduction of what we call today “the lone pair.” Lewis argues: “Important therefore as the chemical bonding pair is to the whole theory of valence, it must be observed that such a pair is not fundamentally different from other pairs which do not act as bonds.” He then depicts the electronic structures of the series, N^{3-} , NH_2^{2-} , NH_2^{1-} , NH_3 , and NH_4^{1+} , and discusses the spatial arrangement of these four pairs, initially in N^{3-} in a symmetric tetrahedral configuration, then as distorted tetrahedral, and finally in NH_4^{1+} again as a symmetric tetrahedron. In many ways, this is a modern description very similar to the VSEPR picture of the effect of lone pairs on geometry.³³

The Nonpolar—Polar Superposition in the Electron Pair Bond

One more step of unification made by Lewis is the merging of the ionic and covalent pictures—one originating in inorganic chemistry by Berzelius and Davy, the other in organic chemistry by the structuralists—into a single bonding picture of an electronic pair that is allowed to move in between the two partners in accord with their relative electronegativities. He specifies: “If a bonding pair is held midway between two like atoms, the molecule is completely nonpolar; if it is shifted in any degree toward one of the atoms, that atom becomes negative in a corresponding degree. When the shift occurs to such a degree that one atom obtains exclusive possession of the pair—which occasionally happens even in a symmetrical molecule . . .—the bond has ceased to exist. The new theory of valence includes as a special case the complete transference of electrons from one atom to another.” This idea looks very much like a precursor of the quantum-based idea of Pauling to describe any bond as a superposition of covalent and ionic forms. In fact, Pauling devised a continuous function of bond ionicity that depends on the electronegativity difference of the two constituent atoms. This function appears in many of the modern periodic tables, and it might be considered as a quantitative articulation of the Lewis polar–nonpolar continuum of electron pair bonding.

Precursor Ideas of Physical Organic Chemistry

It is clear that Lewis views the bond as a dynamic entity, and naturally he considers reactivity of molecules as a reorganization of these electron pairs. Thus, in a bond with high polarity, the pair will move together with the more electronegative atom, while in a homopolar bond, the pair can move with one atom or the other, depending on the conditions. To illustrate this, he discusses “the interesting substance $C_6H_5SO_2OH$, which under certain circumstances hydrolyzes to give phenol and sulphuric acid,

and under others to give benzene and sulphuric acid"; he sees this behavior encoded in the electron-pair structure of the molecule, "for when we see that the bonding pair between phenyl and sulphur may be shifted toward the one or the other, and when the molecule is broken . . ." This is clearly a precursor of the curve arrow, and of the later formulation of heterolytic mechanisms like S_N1 by the Ingold-Hughes school.¹⁸ Indeed, the intense fructifying dialogue that Lewis had with the English school of physical organic chemists can be further noticed, when Lewis discusses the electronic structure of doubly and triply bonded molecules and takes issue with the polar representations of Lowry and others. Thus for example, while Lowry uses a single C—C bond and an ionic distribution of the additional electron pair, $^+C-C^-$, to account for the reactivity of olefins, Lewis favors the doubly bonded representation of ethylene, i.e., $C=C$, since it accounts for the geometric isomers. Nevertheless, he admits that the multiple-bond can be a hybrid of electronic structures. This dialogue will continue and intensify when Ingold will start in 1925 his great work.^{17,18,23,32} Thus while Lewis may have not provided a direct leadership on how to use his ideas for chemical reactivity, he has produced so many pioneering ideas and so many applications that were assimilated in the common chemical consciousness and resprouted in refined and effective ways.

Precursor Ideas of Resonance Theory

Toward the end of his presentation, Lewis discusses conjugation and its relation to tautomerism. He says that normal tautomerism refers to the rapid equilibrium between "two or more distinct substances, to each of which an orthodox formula may be assigned." However, he immediately adds that this is not always the case and refers to experiments by Thorpe and Hantsch, which provide convincing evidence that there are tautomeric situations "that cannot be interpreted by an oscillation between two distinct structures, but rather by a single loose structure of intermediate character." He brings evidence from Hantsch that the acidic hydrogen of carboxylic acid belongs to the two oxygen moieties at the same time and should be drawn connected to both. Isn't this the "classical-nonclassical" debate that erupted a few decades later? Here and elsewhere we can see that Lewis considers "electronic tautomerism" (e.g., when he discusses color of dyes¹³), which is the precursor of the "resonance theory" of Pauling and the "mesomerism" phenomenon of Ingold.

Summary of the Meeting—The Crowned Prophet

In the summary of the Faraday discussion, prepared by Rideal, we find the following statement: "It is to Professor G. N. Lewis that we are indebted for a very valuable conception in that he has given us a visual picture of a mode of union between the atoms alternative to . . . the electron type suggested by Sir J. J. Thomson. . . with the aid of two electrons held in common." Indeed, the influence of Lewis's electron pairing idea pervaded the meeting. Nevertheless, the discussion at this meeting showed that there is more to bonding than an electron pair, as Thomson brought evidence of the molecular ion H_2^+ that is very stable.

Lewis himself recognized the transitory state of his or any theory, and in the introduction to his monograph,³⁰ he writes: "I take it that a monograph of this sort belongs to the ephemeral literature of science. The studied care which is warranted in . . . science would be out of place here. Rather with the pen of a journalist we must attempt to record a momentary phase of current thought, which may at any instant change with kaleidoscopic abruptness." Thus, atypically, Lewis treats his own theory with some aloofness; this is another take home lesson I picked by reading Lewis' work, and comparing it to the subsequently occurring "wars" between proponents of MO and VB theories, and the continuing tendency to adhere to theories a single truths and monologism.³⁴

Post Lewis Descriptions of Electron Pair Bonding

What has occurred in chemical bonding since Lewis? Chemists made wonderful chemistry and extended the bonding types to one-electron and three-electron bonds, and increase the multiple bonding to records of quadruple and now even to quintuple bonds,³⁵ and more (e.g., Cr_2 , U_2). Nevertheless, the electron pair bond of Lewis remains as the single most common quantum of bonding in organic and main element chemistry.

What have we learnt since Lewis about the electron pair bonding? Pauling²⁵ has shown in his valence bond (VB) theory that the bond can be described in terms of resonance between covalent and ionic structures. Molecular orbital (MO) theory can also describe electron pair bonding by transforming the canonical MOs to localized MOs, known as LMOs and which combines two given atoms in a molecule.³⁶ The LMO thus describes the electron pair bond, while the relative coefficients of the atoms that contribute to the LMO describe the bond polarity. Thus both VB and MO theories support the Lewis formulation of the electron pair bond. New theoretical methods based on electron density, Atoms in Molecules (AIM),³⁷ and Electron Localization Function (ELF) based theories³⁸ enable to define the bond by a bond path or a basin, to gauge its electron density ("number of electrons"), its polarity and ionicity. Thus, quantum chemistry supports the Lewis mechanism of bonding and reproduces his key ideas based on solid physical principles.

This state of the notion of bonding may create a sense that there is not much that is new in this field and that our bonding paradigms developed in the past 90 years are quite sufficient for chemistry. Whereas, in part this is true, for the major part this is just a false impression. There is a new generation of chemists who are excited about new problems of chemical bonding. There are also new features of chemical bonding coming from the energy perspective of bonding, e.g., the paradoxical role of the kinetic energy,^{39,40} unusual contribution to bonding revealed by energy partition analysis of bonding,⁴¹ new magic numbers for describing bonding in clusters,⁴² intriguing ideas about the behavior of Lewis structures in high dimensionality,⁴³ and so on and so forth. The VB perspective provides a fresh new look on electron pair bonding, showing that there is a large group of bonds both homonuclear and heteronuclear, so called charge-shift bonds,⁴⁴ where the bonding does not originate in the spin-pairing of the electrons or in the electrostatic interaction

between the atoms, but rather in the resonance energy between the ionic and covalent constituents of the bond. Such covalent–ionic fluctuation energy holds, for example, the two fluorine atoms in F_2 and many other molecules including most transition metal complexes. Charge-shift bonding is associated with a number of experimental phenomena, and most recently it has been demonstrated that the covalent ionic resonance energy of these bonds is a chemical observable.⁴⁵ Another interesting bonding mechanism comes from triplet electron pairs, as is manifested in maximum spin clusters of monovalent atoms, like $n+1Li_n$, $n+1Cu_n$, and so on.^{46–49} The bonding in this clusters arises from the covalent–ionic fluctuation of the triplet pair and is able to sustain large clusters with high magneticity,^{48,49} looking like Bose–Einstein condensates but bonded by rather strong forces that amount to as much as 19 kcal/mol per a single atom.⁴⁹ New fundamental bonding paradigms may arise from new fast laser techniques of femto- and attoseconds, when the electronic time-scale will be probed⁵⁰; many molecular species with loose electrons that can lead to fluctuation between forms⁵¹ are awaiting to be probed. Fuller understanding is required of “metallic bonding”⁵² and its more precise connection to bonding in molecules like benzene, and so on.⁵³ The conclusion must be then that this chemical territory is not barren; it still fertile and teaming with bonding problems to be tackled in new materials, nanoparticles,⁵⁴ quantum dots, metalloenzymes,^{55,56} and so on and so forth.

Conclusion

Lewis was the initiator of the “electronic structure revolution” and the founder of the chemical territory “the chemical bond”—the element from which we construct a chemical universe. The strength of his hypothesis rested on a wide-ranging experimental foundation, following the maxim of Roald Hoffmann: “Experimental trends are noted. A theory is constructed that does not merely rationalize but makes verifiable predictions. When these predictions fail the theory can be enriched by reexamination. Chemistry advances.”⁵⁷ Indeed, such as this was the Lewis theory, and hence, his ideas and applications have resurfaced in modern approaches to the chemical bond; the covalent–ionic superposition theory of bonding and resonance theory, mesomerism, inductive effects, and VSEPR rules. His analysis of reactivity of bonds formed a basis for modern physical organic chemistry. Nevertheless, despite the feeling this may give us that there is nothing new under the sun, one can argue that the chemical territory is exploding with problems to be solved! The dialog of chemists with the notion of the chemical bond continues. . . .⁵⁸

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References

1. Bensaude-Vincent, B.; Stengers, I. *A History of Chemistry* (van Dam, D., English translation); Harvard University Press: Cambridge, 1996; (a) *ibid.*, p. 245; (b) *ibid.*, p. 206; (c) Knight, D. *Ideas in Chemistry: A History of Science*; Rutgers University Press: New Brunswick, NJ, 1992, Ch. 13.
2. Ritter, S. K. *Chemistry and Engineering News*, 29th Issue; November 2004, p. 31.
3. Siegfried, R. *From Elements to Atoms: A History of Chemical Composition*; American Philosophical Society: Philadelphia, 2002; p. 16.
4. Roob, A. *The Hermetic Museum: Alchemy and Mysticism* (White-side, S., English translation); Taschen Verlag GmbH: London, 1997; p. 132.
5. Lemery, N. A. *Course of Chymistry* (4th English Edition translated from the French edition of 1715); London, 1720.
6. Klein, U. *Ambix* 1995, 42, 79.
7. Macquer, P.-J. *Elements of the Theory and Practice of Chemistry* (Reid, A., English translation), Vol. 1, 2; London, 1758.
8. Noyes, W. A. *J Am Chem Soc* 1917, 39, 879.
9. Chayut, M. *Ann Sci* 1991, 48, 527.
10. Thomson, J. J. *Philos Mag J Sci* 1914, 27, 757.
11. Servos, J. W. *Physical Chemistry from Ostwald to Pauling*; Princeton University Press: Princeton, 1990; p. 4.
12. Servos, J. W. *J Chem Educ* 1984, 61, 5.
13. Lewis, G. N. *J Am Chem Soc* 1916, 38, 762.
14. (a) Heitler, W.; London, F. *Zeits für Physik* 1927, 44, 455; (b) Heitler, W.; London, F. *Quantum Chemistry Classic Scientific Paper* (Hettema, H. English Translation); World Scientific: Singapore, 2000, p. 140.
15. Pauling, L. *Proc Natl Acad Sci USA* 1928, 14, 359.
16. Slater, J. C. *Phys Rev* 1931, 37, 481.
17. Davenport, D. A. *Bull Hist Chem* 1996, 19, 13.
18. Calvin, M. *J Chem Educ* 1984, 61, 14.
19. Langmuir, I. *J Am Chem Soc* 1919, 41, 868.
20. Jensen, W. B. *J Chem Educ* 1984, 61, 191.
21. Nye, M. J. *From Chemical Philosophy to Theoretical Chemistry*; University of California Press: Los Angeles, 1993; p. 186.
22. London, F. Z. *Physics* 1928, 46, 455.
23. Saltzman, M. D. *Bull Hist Chem* 1996, 19, 25.
24. Gavroglu, K.; Simoes, A. *Stud Biol Phys Sci* 1994, 25, 47.
25. Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1939.
26. Hager, T. *Force of Nature: The Life of Linus Pauling*; Simon and Schuster: New York, 1995; p. 63.
27. Lewis, G. N. *J Am Chem Soc* 1913, 35, 1448.
28. Lewis, G. N. *Trans Faraday Soc* 1923, 19, 450.
29. Bray, W. C.; Branch, G. E. K. *J Am Chem Soc* 1913, 35, 1440.
30. Lewis, G. N. *Valence and the Structure of Atoms and Molecules*; The Catalog Company: New York, 1923.
31. Stranges, A. N. *J Chem Educ* 1984, 6, 185.
32. Jensen, W. B. *Bull Hist Chem* 1992/1993, 13/14, 47.
33. Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometry*; Oxford University Press: London, 2001.
34. Hoffmann, R.; Shaik, S.; Hiberty, P. C. *Acc Chem Res* 2003, 36, 750.
35. Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettingner, J. C.; Long, G. J.; Power, P. P. *Science* 2005, 310, 844.

36. (a) Edmiston, C.; Ruendenberg, K. *Rev Mol Phys* 1963, 35, 457; (b) Boys, S. F. In *Quantum Theory of Atoms, Molecules, and the Solid State*; Löwdin, P.O., Ed.; Academic Press: New York, 1968; p. 253.
37. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.
38. Silvi, B. *J Phys Chem A* 2003, 107, 3081.
39. Ruedenberg, K. *Rev Mod Phys* 1962, 34, 326.
40. Kutzelnigg, W. In *Theoretical Models of Chemical Bonding*, Vol. 2; Maksic, Z. B., Ed.; Springer-Verlag: New York, p. 1.
41. Kovacs, A.; Esterhuysen, C.; Frenking, G. *Chem Eur J* 2005, 11, 1813.
42. Balakrishnamurajan, M. M.; Jemmis, E. D. *J Am Chem Soc* 2000, 122, 456.
43. Frantz, D. D.; Herschbach, D. R. *Chem Phys* 1988, 126, 59.
44. Shaik, S.; Danovich, D.; Silvi, B.; Lauvergnat, D. L.; Hiberty, P. C. *Chem Eur J* 2005, 11, 6358.
45. Hiberty, P. C.; Megret, C.; Song, L.; Wu, W.; Shaik, S. *J Am Chem Soc* 2006, 128, 2836.
46. McAdon, M. H.; Goddard, W. A., III. *J Phys Chem* 1988, 92, 1352.
47. Glukhovtsev, M. N.; von Rague Schleyerqq, P. *Isr J Chem* 1993, 33, 455.
48. de Visser, S. P.; Danovich, D.; Wu, W.; Shaik, S. *J Phys Chem A* 2002, 106, 4961.
49. de Visser, S. P.; Wu, W.; Danovich, D.; Danovich, M.; Shaik, S. *J Phys Chem* 2006, 110, 8510.
50. Schwarz, W. H. E. *Angew Chem Int Ed* 2006, 45, 1508.
51. Schafer, H.; Eisenmann, B.; Muller, W. *Angew Chem Int Ed* 1973, 12, 694.
52. Anderson, W. P.; Burdett, J. K.; Czech, P. T. *J Am Chem Soc* 1994, 116, 8808.
53. Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem Rev* 2001, 101, 1501.
54. (a) Staszewska, G.; Staszewski, P.; Schultz, N. E.; Truhlar, D. G. *Phys Rev B* 2005, 71, 045423; (b) Schultz, N. E.; Staszewska, G.; Staszewski, P.; Truhlar, D. G. *J Phys Chem B* 2004, 108, 4850.
55. Ogliaro, F.; Cohen, S.; de Visser, S. P.; Shaik, S. *J Am Chem Soc* 2000, 122, 12892.
56. Ogliaro, F.; Cohen, S.; Filatov, M.; Harris, N.; Shaik, S. *Angew Chem Int Ed* 2000, 39, 3851.
57. Hoffmann, R. In *Aspects de la Chimie Quantique Contemporaine*; Daudel, R.; Pullman, A., Eds.; CNRS: Paris, 1971; pp 133–164.
58. Burdett, J. K. *Chemical Bonds: A Dialog*; Wiley: New York, 1997.