

The chemists' electron

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Abstract. This paper narrates the way chemists have been using the electron to account for one of the most intriguing problems, namely the bonding of two neutral atoms to form a molecule. The chemists' attempts to account for the mechanism of the homopolar bond, first in the context of the old quantum theory and after 1926 in the context of wave mechanics, brought the specter of reductionism to physics. We argue that the chemists' successful appropriation of the electron strengthened, first, the autonomy of physical chemistry and, then, of quantum chemistry with respect to physics.

Résumé. Dans cet article on narre comment l'électron avait été utilisé par les chimistes, afin de rendre compte d'un problème intrigant, notamment celui de la liaison de deux atomes neutres pour former une molécule. Les efforts des chimistes de rendre compte du mécanisme de la liaison homopolaire, d'abord dans le contexte de la théorie quantique ancienne, ensuite, après 1926, dans le contexte de la mécanique ondulatoire, a fait entrer dans la Physique le spectre du réductionnisme. Nous soutenons la thèse que l'appropriation réussie de l'électron par les chimistes a renforcé l'autonomie, par rapport à la Physique, d'abord de la chimie physique et, ensuite, de la chimie quantique.

1. Introduction

The aim of Robert Millikan's Faraday lecture before the members of the Chemical Society on June 12, 1924 was to convince his chemical audience that the electron 'is a definitely and directly observable fact' [1], attempting throughout his presentation 'to differentiate . . . between . . . fact and . . . fancy' [2]. Even though no one, according to Millikan, could doubt the atomicity of electric charge, there was considerable disagreement between chemists and physicists about the behaviour of atomic charges inside of the atom. In particular, the controversy concerned 'how the electrons spend their leisure time, the portions of their lives within the atom when they are not radiating' [3].

2. Whose was the atom, anyway?

Such disagreement was not new between the physicists and chemists. Since the mid-1890s British chemists, in particular, were attempting to re-appropriate a concept which had been 'snatched' from them by their fellow physicists. British chemists, during the 1880s, were expressing an increasing interest in the possibilities provided by the dynamic approach of British physicists to understand the details of the behaviour of atoms. But the views put forth by the energeticists, the various developments in chemistry where the use of mathematics became a necessary ingredient for doing chemistry, and the developments in physics where the understanding of the behaviour of the atoms was achieved at the expense of the 'billiard ball' ontology,

which was so appealing to the chemists, obliged the chemists to re-acquisition what they felt was theirs in the first place. Thus, British chemists found themselves between a world of ethereal vortices articulated by their fellow physicists and a world of anti-atomic energetics propagandized by German physical chemists.

By the late 1870s the atom, a chemical entity *par excellence*, had been quite successfully appropriated by the physicists. It was not until the mid-1890s that the chemists started to re-assert their lost jurisdiction over atomic theory [4]. The prospects promised by the early successes of the dynamical approach did not leave the chemists uninterested. In fact, in the early 1880s it appeared that dynamical theory may even provide an explanation of why atoms are held together to form a molecule. In 1883 J J Thomson had shown that a complex mechanism of vortex rings could account for the mechanism of valence and proposed that, if vortex rings are considered as atoms, then the chemical combination of elements can be viewed as the pairing of such vortex rings [5]. Many of the dominant figures of the chemical establishment, during their public lectures, overemphasized the need for cooperation with the physicists. Roscoe in 1884 stressed that one 'of the noteworthy features of chemical progress is the interest taken by physicists in fundamental questions of our science' [6]. In 1885 Henry Armstrong discussed one of the cardinal issues of chemistry, which was the understanding of the nature of chemical change, a subject which, he emphasized, 'requires the immediate earnest attention of chemists and physicists' [7]. In 1888 J J Thomson published his lecture notes at the Cavendish under the title *Applications of Dynamics to Physics and*

Chemistry. Although chemistry was cruelly reduced to physics, there did emerge a dynamical framework which could accommodate the physical *and* chemical phenomena together. In 1893 Emerson Reynolds placed great emphasis on what he called 'physico-chemical' problems. In 1895 Ralph Meldola argued that the 'one great desideratum of modern chemistry is unquestionably a physical or mechanical interpretation of the combining capacities of atoms' [8]. But all this talk came to an abrupt end in 1896, the year Wilhelm Ostwald launched his campaign for energetics at the Lübeck meeting of the Society of German Scientists and Physicists.

Soon afterwards, some British chemists started to go on the offensive. In 1902 Edward Divers, who was the vice-president of the Chemical Society, delivered the presidential address to the chemical section of the British Association for the Advancement of Science (BAAS). His grudge was against the physicists who had never been 'satisfied with the hard, indivisible ball of specific substance and definite mass which has served chemistry so well'. He denounced the physicists who had manipulated the atom, making, in fact, 'even a vortex ring of it'. Divers' main thrust was that all this meddling with the atom led to a situation that only a 'few chemists can understand' [9]. In contrast to the physicists' practice, the chemists had not meddled with the atom's interior. Divers argued that chemistry dealt with tangible truths and did not need the help of mechanical models in order to legitimate its various laws.

In 1906, two years after his Faraday Lecture in London, Ostwald indicated that he was having second thoughts about his denial of the existence of atoms. The next year, Arthur Smithells, the forceful spokesman of British chemistry, was telling his audience at the annual BAAS meeting that, when compared to 20 years ago, everything appeared to be more promising in chemistry. Although the discovery of radioactivity did mark a new epoch in the history of chemistry, there did not appear to be any reasons to start questioning any of the constitutive aspects of chemistry. His pronouncement was that the chemists were perplexed, not so much by the new ideas, but by the invasion 'of chemistry by mathematics'. It appeared that chemists were feeling 'submerged and perishing in the great tide of physical chemistry which was rolling up into our laboratories' [10]. Smithells concluded by commanding that chemistry should not be invaded by mathematical theorists!

In 1909 Henry Armstrong pursued the same aggressive strand. Concerning his views about the energeticists, Armstrong boasted that, even though his attitude was one of 'complete antagonism towards the speculations of the Ostwald school', he claimed, nevertheless, to have been the first English chemist to publicly remark that Ostwald's investigations were of the highest importance. But now Ostwald had changed his mind, and Armstrong warned his fellow chemists in a most dogmatic manner about the dangers of dogmatism.

He reminded his audience how Ostwald had 'charged his test tubes with ink instead of chemical agents' and how he tried to convince chemists to become adherents of the cult of his school. He warned his audience of the dangers 'of uncontrolled literary propagandism in science'. But that was not the end. Armstrong had one more account to settle. He appealed to the physicists to make themselves more acquainted with the methods of the chemists and to stop speculating unnecessarily. He felt that such an attitude by the physicists was all the more necessary, especially since they appeared to 'dictate a policy' to the chemists, without making much effort to understand their methods of 'arriving at the root conceptions of structure and the properties as conditioned by structure. It is a serious matter that chemistry should be so neglected by physicists' [11].

It was Joseph Larmor's *Aether and Matter* which, more than any other work, can be considered as being a concrete response to the necessity for a consensual theoretical framework for both the physicists and the chemists. It was published in 1900 and was substantially the same text for which he had been awarded the Adams Prize two years earlier. Larmor's work was a study of the relations of 'microdiscontinuity to macrocontinuity' [12] and his ether attempted to play a unifying role, explaining all natural phenomena. Electromagnetism could no longer be considered as being solely based on the idea of the continuum without the necessary changes due to microscopic considerations after the discovery of the electron.

It should be stressed that even though Larmor's *Aether and Matter* was motivated by and aimed at the problems with electromagnetism, it does afford a chemical reading and chemical considerations were a significant contributory factor for its completion. Larmor was quite knowledgeable about various chemical problems and especially about chemical affinity. Ten years earlier in the introduction of his *A Treatise on the Motion of Vortex Rings* J J Thomson had thanked Larmor for his 'valuable suggestions' and soon afterwards Larmor had produced his own theory to account for chemical phenomena. 'I am now deep into atomism' he wrote to Oliver Lodge in 1894 [13].

Aether and Matter attempted to create a consensus not only on the issue of ontological commitments, but on the issue of methodological preferences as well. It would not be unreasonable to assume that Larmor was pursuing an agenda in which the ontological issues that had to be settled between the physicists and the chemists were closely related with the methodological issues involved in setting up a consensual theoretical framework. Decisions about the former necessitated decisions about the latter. The new consensus was not only a matter of devising a new theory as such, but of articulating the novelty of the theoretical *approach* as well.

It is also possible to narrate the conflict between the two different conceptions of the atom, the physicists' dynamic atom and the chemists' static atom, as a clash between two different conceptions of the electron. Even

though the clash dates from before the ‘discovery’ of the electron [14], after that ‘discovery’ it was transformed to a conflict between two incompatible conceptions of the electron. The incompatibility between the physicists’ dynamic atom and the chemists’ static atom became a mere epiphenomenon of an underlying conflict between the physicists’ and the chemists’ electrons. We do not mean to suggest that the ‘discovery of the electron’ was an unproblematic and straightforward event. Despite its complexity, however, the process which has been seen retrospectively as the ‘discovery of the electron’ rendered the incompatibility between the two atoms an epiphenomenon of the incompatibility between their respective subatomic constituents. A dynamic atom resulted from a non-magnetic electron which obeyed Coulomb’s law (except in quantum transitions), whereas a static atom resulted from a magnetic electron which (at small distances) violated Coulomb’s law. Furthermore, chemists were not very interested in detailed pictures of the structure of the atom; they were, rather, concerned with ‘an atom’s outermost electrons’, the only electrons which entered in the process of chemical combination [15]. As J J Thomson remarked in 1923, ‘the electron is the dominating factor in these problems which are just those with which the chemist is most concerned’ [16].

We shall attempt to narrate parts of this conflict, in terms of the different methodological outlook of two distinct scientific cultures, the physicists and the chemists.

3. Emergence of the conflict: G N Lewis’s loafer electron

Gilbert N Lewis (1875–1946) [17] commenced his graduate studies at Harvard in 1897 and was trained by the physical chemist T W Richards. In 1900, a year after he had completed his dissertation, he went to Germany and worked with Ostwald and Nernst. The instrumentalism that pervades his mature writings can be traced, perhaps, to his early interaction with Ostwald. Lewis’s radical instrumentalism was displayed in his *Valence and the Structure of Atoms and Molecules* [18] where he argued that the empirical success of Bohr’s model of the hydrogen atom did not provide adequate grounds for believing that it was ‘something more than a mere working hypothesis, and may represent an ultimate reality’.

Lewis is best known for his proposal that electron pairs can account for the homopolar bond between atoms. The new ideas on the electronic constitution of matter along with the periodic properties of the chemical elements were the central elements of his problem situation. The two main *desiderata* were to portray the atom as composed primarily of electrons [19] and to provide a physical interpretation, based on the new model of the atom, of the periodic table. Both of these *desiderata* were fulfilled with Lewis’s 1902 proposal of a cubic atom. According to that proposal, the atom had an elaborate cubic structure and was composed of

electrons which occupied the vertices of a series of concentric cubes. The most important aspect of that theory was that it portrayed the electron within the atom as a static particle to suit the chemical static atom.

The next stage in his development of the theory began in 1916. In the meantime several developments had taken place in both chemistry and physics which were decisive for the further elaboration of the 1902 theory. In 1904 Richard Abegg (1869–1910) had proposed a new interpretation of valence based on the recently ‘discovered’ electron [20]. Before the advent of the electron ‘the valence of an atom... was defined as the number of bonds which attach it to other atoms’ [21]. In Abegg’s theory the ‘normal’ valence of an atom amounted to the definite number of electrons that the atom would give (positive valence) or take (negative valence) upon its combination with another atom to form a molecule or a compound. Further details of Abegg’s scheme need not concern us here. Suffice it to say that for him the affinity between two atoms was a purely electrostatic phenomenon due to the transfer of electron(s) from one atom to another and the concomitant electrostatic attraction between the oppositely charged atoms.

In the same year that Abegg published his theory of electrovalence J J Thomson proposed the ‘plum pudding’ model of the atom, in which corpuscles (electrons) moved in coplanar, circular orbits inside a homogeneously and positively charged sphere [22]. Thomson’s model provided a qualitative understanding of the periodic table of Mendeleev and of chemical combination, among other phenomena. The demand for a mechanically stable atom, formulated in terms of Thomson’s model, provided the key for the interpretation of the periodic properties of the elements. Only those rings of corpuscles which contained a number of corpuscles below a certain threshold would be stable. Above that threshold a ring would break into two distinct rings, the additional ring being formed from the extra electrons which threatened the stability of the previous ring. Since the chemical properties of the elements were determined by those extra electrons, a periodic occurrence of the same number of electrons in the ‘incomplete’ ring of different elements would result in the periodicity of their chemical properties.

In 1907 Thomson developed further the chemical applications of his atomic theory in a highly influential book, *The Corpuscular Theory of Matter* [23]. Again, despite the theoretical possibility of non-polar bonds (i.e. bonds ‘binding the two systems together without a resultant charge on either system’ [24]), Thomson only admitted the existence of polar bonds ‘established between two atoms [by] the transference of one corpuscle from the one atom to the other’ [25]. In the 1910s, due to the popularity of Thomson’s theory among American chemists, the exclusive reality of polar bonds became part of the orthodoxy of the day.

It is ironic that Thomson became one of the first to revolt against the orthodoxy that his 1907 theory had helped to consolidate. In 1914 he published a paper in

which he admitted the existence of two kinds of bonds, polar and non-polar [26]. In non-polar bonds there was no electron transfer between the atoms forming the chemical compound. Instead, such bonds consisted of two tubes of force, one between an electron of the first atom and the nucleus of the second and another between an electron of the second atom and the nucleus of the first [27]. The important innovation of Thomson's paper that proved significant for Lewis's further elaboration of his cubic atom was the idea that a pair of electrons was involved in a non-polar bond [28].

Another crucial development that formed part of Lewis's problem situation was Parson's proposal in 1915 of an electron endowed with magnetic properties [29]. Parson portrayed the electron as a revolving circular band of negative electricity which, as a result of its rotation, had a magnetic moment and was, thus, called 'magneton'. Parson had not been the first to associate magnetic properties with the electron. Ten years before Parson's proposal and in a different context the French physicist P Langevin (1872–1946) had considered the electron as the ultimate magnetic particle [30]. The important innovation of Parson, however, was the utilization of his magnetic electron for understanding the process of chemical bonding.

Parson had shown his paper, prior to its publication, to Lewis and, thus, stimulated Lewis to revive his 1902 theory. The most important aspect of Parson's paper *vis-a-vis* the development of Lewis's theory was a new mechanism of chemical binding based on the magnetic properties of the electron. The then dominant conception of chemical bonding portrayed the formation of chemical compounds as due exclusively to the transfer of electrons from one atom to another and the concomitant electrostatic attraction between the oppositely charged atoms. That theory of chemical bonding, however, could not explain the formation of molecules consisting of neutral parts, like the hydrogen molecule (H_2) and the majority of organic compounds. Due to these difficulties the view that the only mechanism of chemical bonding was a process of electron transfer had been already challenged. A group of chemists at Berkeley, under the leadership of G N Lewis, 'suggested that there are two distinct types of union between atoms: polar, in which an electron has passed from one atom to the other, and non-polar, in which there is no motion of an electron' [31]. No physical mechanism was proposed, however, to account for the formation of non-polar bonds. It was this elusive mechanism that Parson supplied in his 1915 paper.

Like J J Thomson, Lewis and his colleagues, Parson admitted the existence of two kinds of bonds, polar and non-polar. Unlike polar bonds, which were formed by magneton transfer, non-polar bonds consisted of a pair of magnetons which was formed as a result of the magnetic attraction between two magnetic electrons, an attraction strong enough to overcome the electrostatic repulsion between the negatively charged particles. It was, thus, the magnetic character of Parson's electron that enabled the formation of non-polar bonds. Parson's

idea of a magnetic electron was a significant resource for the subsequent development of Lewis's theory of atomic structure.

The most innovative aspect of that development was Lewis's idea that the chemical bond between two atoms in a molecule consisted of a *pair* of electrons that did not belong exclusively to either of the combining atoms but were, instead, shared by both of them. It appears quite plausible that Lewis derived the shared pair bond in 'some way from the rich and suggestive speculations of Thomson... and Parson on the non-polar bond' [32]. Lewis had already introduced the distinction between polar and non-polar bonds in 1913 but he had not offered any physical mechanism that could account for the formation of non-polar bonds. Such a mechanism was provided by Thomson in 1914 and by Parson in 1915. The problem then facing Lewis was to translate Thomson's and Parson's conceptions into the terms of his 1902 cubic model of the atom and to retain only those aspects of their theories that could fit into his own theory of atomic structure. We will discuss Lewis's seminal paper 'The atom and the molecule' [33] and the problems that it tried to address, while at the same time, exhibiting the features of Lewis's conception of the electron that conflicted with those ascribed to it by the physicists.

Whatever its origins, the cubic model of the atom seemed to Lewis 'more probable intrinsically than some of the other theories of atomic structure which have been proposed' [34]. Lewis's atom consisted of a core of negative and positive charges that did not partake in chemical phenomena and an outer shell of electrons that governed chemical changes. The net positive charge of the inner core was balanced by the negative charge of the outer shell so that the atom as a whole was electrically neutral. The model portrayed the electrons as static particles which, moreover, did not strictly obey Coulomb's law. As Lewis remarked, 'Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances' [35].

It is important to reconstruct the reasoning that led Lewis to abandon the unrestricted validity of Coulomb's law in order to see in what respects the physicists' electron, invariably subject to Coulomb's inverse square formula, was an obstacle for the understanding of chemical phenomena. There were two ways, according to Lewis,

... in which one body can be held by another. It may, owing to a force of attraction, be drawn toward the second body until this force is gradually offset by a more rapidly increasing force of repulsion. In this case it comes to rest at a point where the net attraction or repulsion is zero... [36]

This was exactly the way in which electrons were held together in the atom, presumably under the attractive–repulsive action of the positive charges that were also in the atom and under their own mutual repulsion–attraction [37]. It should be emphasized that Lewis

kept silent about the nature and arrangement of the positive charges inside an atom and he did not offer any mathematically formulated alternative to Coulomb's law. As a result he was unable to show that the cubical structure and the stability of his atom followed from the collective interaction between electrons and positive charges. The qualitative nature of Lewis's model of the atom explains, to some degree, why it was not taken very seriously by the physicists [38].

The second way in which the electrons could be held together in the atom was the physicists' way, most notably Rutherford's. According to that model electrons were revolving around a massive, positively charged nucleus under the action of an inverse square, attractive force. Rutherford did not make any attempt to employ his model in order to explain the chemical properties of the elements and, not surprisingly, his theory did not appeal to chemists. As Lewis remarked, the so-called 'planetary' model of the atom

...seems inadequate to explain even the simplest chemical properties of the atom, and I imagine it has been introduced only for the sake of maintaining the laws of electromagnetics which are known to be valid at large distances [39].

Furthermore, the advantage of 'maintaining the laws of electromagnetics' was not preserved in the most sophisticated among the planetary models, namely Bohr's semi-classical model. Bohr's dynamic electron violated classical electromagnetic theory in two respects. First, it was influenced by Coulomb forces only when 'the angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value [$h/2p$; where h is Planck's constant], independent of the charge on the nucleus' [40]. Second, in these 'stationary' states the electron violated classical electrodynamics, since it did not emit radiation.

Lewis diagnosed another respect in which Bohr's dynamic electron was incompatible with contemporary electromagnetic theory. The motion of Bohr's electrons

...produces no effect upon external charges. Now this is not only inconsistent with the accepted laws of electromagnetics but, I may add, is logically objectionable, for that state of motion which produces no physical effect whatsoever may better be called a state of rest. [41]

It is not clear from the above passage what, exactly, was Lewis's objection against Bohr's theory. Lewis, however, developed that objection in a paper that was published the following year [42]. In that paper he exposed a hidden consequence of Bohr's model of the atom through the following thought experiment:

Let us... represent a hydrogen atom according to Bohr with an electron in the first orbit [by a circle whose diameter is XX'], that is to say in the most stable state, and let us represent by AA' a small wire which may be brought near to the hydrogen atom [parallel to

XX']. Now if the electron in the orbit exerts any sort of electrical force at a distance, when the electron is in position X there will be a slight flow of positive electricity in the wire toward A , and when the electron is at X' there will be a slight flow toward A' . Indeed at any finite distance of the wire from the atom there should be set up in the wire a finite alternating current which would continue indefinitely. Such a current should generate heat, but since the atom is supposed to be in the state of lowest possible energy there appears to be no source from which the heat could originate. In other words, we must conclude either that such an alternating current is not produced or that it is produced but meets with no ohmic resistance [43].

Lewis eliminated the second alternative on experimental grounds and concluded that 'an electron, in a Bohr orbit, exerts upon other electrons no force which depends upon its position in the orbit' [44]. That conclusion was an essential step towards the reconciliation of Bohr's dynamic and Lewis's static electron and will be further discussed below.

Thus, in Lewis's view, the physicists' dynamic electron was not only incompatible with chemical data but also objectionable on 'logical' grounds. Moreover, he claimed that the predictive success of Bohr's theory *vis-a-vis* the lines of the hydrogen spectrum could be duplicated by his own model if one assumed 'that an electron may be held in the atom in stable equilibrium in a series of different positions, each of which having definite constraints, corresponds to a definite frequency of the electron' [45]. It is evident that Lewis proposed a totally classical picture of the electron which dispensed with quantum conditions. As we will see, this was one of the sources of resistance to Lewis's proposal by those physicists that were engaged with the development of quantum theory.

So far we have identified three characteristics of Lewis's model that might have led to its less than enthusiastic support by the physics community: first, its qualitative, non-mathematical formulation [46]; second, its disregard for quantum conditions; and third, its violation of the strict validity of Coulomb's law. That final feature of Lewis's theory was closely related with the magnetic properties of the electron. If the electron was a tiny magnet, as Parson had suggested in 1915, the configuration of electrons inside the atom would be the product of the operation of magnetic forces, in addition to the operation of Coulomb-like electric forces. The repulsive, inverse square force between two electrons would be counteracted by an attractive, magnetic force. Assuming the existence of such forces, Lewis stated that Parson had been led to a similar conclusion as his: the most stable condition for the atomic shell is the one in which eight electrons are held at the corners of a cube [47]. Thus, Parson's attribution of magnetic properties to the electron explained why electrons did not strictly obey Coulomb's law and thus justified on physical grounds a crucial aspect of Lewis's theory. It should be noted, however, that, contrary to Lewis's claims, Parson

had not been able to demonstrate mathematically that a cubic arrangement of electrons inside the atom followed from the combined action of electric and magnetic forces [48].

The idea of a magnetic electron also enabled another crucial innovation that Lewis introduced in 1916, namely the conception of the chemical bond as consisting of a pair of electrons shared between the combined atoms [49]. The two electrons occupied the vertices of an edge that was common to both cubic atoms. A chemical bond of this kind would not have been possible if the only force acting between two electrons was electrostatic repulsion. A magnetic force was necessary to overcome that repulsion and draw the two particles together.

Finally, the magnetic electron was essential for the representation of the triple bond, i.e. the bond between two atoms that shared three pairs of electrons. From a geometrical point of view two cubic atoms could never share three pairs of electrons. The pictorial representation of the triple bond requires that the combined atoms possess a tetrahedral structure. A cubic structure can be transformed to a tetrahedral one if 'each pair of electrons [that occupy the vertices of the cube] has a tendency to be drawn together, perhaps by magnetic force', a tendency that can be reasonably assumed 'in such very small atoms as that of carbon'. The tetrahedral structure, moreover, 'explains the phenomenon of free mobility about a single bond which must always be assumed in stereochemistry' [50].

4. Irving Langmuir's elaboration of Lewis's ideas

In 1903 Irving Langmuir (1881–1957) obtained his degree in metallurgical engineering from the School of Mines at Columbia University [51]. He entered the School of Mines because, as he remarked later, 'the course was strong in chemistry' and, moreover, 'it had more physics than the chemical course, and more mathematics than the course in physics—and I wanted all three' [52]. After the completion of his undergraduate studies, he went to Germany and worked with Walther Nernst 'on the dissociation of various gases by a glowing platinum wire, research that became the topic of his 1906 doctoral dissertation' [53]. In 1906 he returned to the United States and began his career first at the Stevens Institute of Technology and, then, at the new research laboratory of General Electric in Schenectady, New York. The laboratory in Schenectady provided an ideal research environment and Langmuir stayed there until his retirement in 1950.

According to Robert Kohler, who has reconstructed in detail the origins of Langmuir's concern with atomic structure [54], Langmuir had been interested in atomic models since 1916. As his notebooks from that period reveal, he 'thought that there were better theories than Bohr's, such as Alfred Parson's magneton theory which he had just been studying'. Furthermore, he

agreed with G N Lewis that Bohr's model of the atom 'ignored the facts of stereochemistry...[and] was designed simply to 'save Coulomb's Law' at short distances' [55]. His negative appraisal of Bohr's atomic theory contrasted with his favourable view of Lewis's static model of the atom. Thus, Lewis's atomic theory along with Parson's proposal of an electron endowed with magnetic properties were important resources upon which Langmuir drew for the development of his own theory of atomic structure. A further element of his problem situation was his hope to create 'a new chemistry, a deductive chemistry, one in which we can reason out chemical relationships without falling back on chemical intuitions' [56].

A preliminary version of his theory appeared in the 1919 issue of the *Proceedings of the National Academy of Science* [57]. In the beginning of his article Langmuir acknowledged that 'this theory, which assumes an atom of the Rutherford type...is essentially an extension of Lewis's theory of the 'cubical atom...'. He continued by laying out his theory in terms of eight postulates, a form of exposition that betrays his ideal of a 'deductive chemistry'. The first postulate asserted that 'the electrons in atoms are *either stationary or rotate, revolve or oscillate about definite positions in the atom*' [58]. (Emphasis added.) It should be emphasized that Langmuir's model of the atom, in contrast with Lewis's, was not based on the assumption of a completely stationary electron. Rather, it was compatible with the supposition of a dynamic electron. Langmuir modified Lewis's theory in order to reconcile it with Bohr's model of the atom, which, as we mentioned above, was based on the assumption of a rapidly moving electron.

The first postulate also included a symmetry principle, according to which 'The electrons in the...atoms...of the inert gases, have positions symmetrical with respect to a plane called the equatorial plane, passing through the nucleus at the center of the atom'. The second postulate stated that the electrons in atoms are distributed in successive 'concentric (nearly) spherical shells, all of equal thickness'. Moreover, the 'mean radii of the shells form an arithmetic series 1, 2, 3, 4, and the effective areas are in the ratios 1 : 2² : 3² : 4²'. Each of those shells was divided, according to the third postulate, 'into cellular spaces or cells occupying equal areas in their respective shells and distributed over the surface of the shells according to the symmetry required by postulate 1'. Thus, the first shell should contain two cells (one above and one below the equatorial plane), the second, having an area four times larger than the first, should contain eight cells, and so on. The cells in the first shell are occupied, according to the fourth postulate, by a single electron; while cells in successive shells can contain, at most, two electrons. The latter are allowed to contain two electrons only if every other cell in the same shell is occupied by, at least, one electron. Furthermore, electrons start to populate a shell only after all previous shells get 'their full quotas of electrons'. The fifth postulate capitalizes on the magnetic properties of the electron to determine the arrangement of electrons

in the outermost shell. These electrons are subject to a magnetic attraction from the 'underlying' electrons. When the number of the outside electrons is small this magnetic attraction predominates over the electrostatic repulsion (also due to the underlying electrons) and determines their arrangement. When, on the other hand, there are many outside electrons the electrostatic repulsion becomes dominant and pushes them 'as far as possible from the underlying ones'. Postulates six and seven concern the stability of electronic arrangements. The former asserts that a pair of electrons (e.g. in the helium atom) is the most stable grouping of electrons; while, according to the latter, 'the next most stable arrangement of electrons is the octet [a group of eight electrons]' [59]. Finally, the eighth postulate introduces the idea that an electron (or a pair of electrons) can be shared by, at most, two octets.

By means of those postulates Langmuir could explain the chemical properties of all the elements. Whereas Lewis's theory

... could be used to explain the *physical* and chemical properties of the first twenty elements.... I have been able to extend the theory to cover all the elements and to give a theory of the mechanism of chemical combination which gives a rational explanation of most of the very varied and extensive data underlying the Periodic Table and the different theories of valence [60].

The breadth and empirical success of Langmuir's theory, as well as the fact that he was equally at home in academic and in industrial chemistry, facilitated the reception of Lewis's ideas by the community of chemists, which had a significant industrial component [61].

5. The Faraday Society meeting of 1923

In 1923, after the publication of Lewis's book, there was a meeting organized by the Faraday Society at the University of Cambridge which dealt with the 'Electronic theory of valency'. J J Thomson was the Chairman of the meeting and his opening statement was a particularly succinct formulation of the tasks awaiting the chemists. 'The bond dominates the field of chemistry, which finds its most suggestive mode of expression in terms of electrons. Admitting the presence of electrons, their repulsion involves important chemical consequences' [62].

Lewis gave the introductory talk and though he felt that the meeting's aim was to secure a better mutual understanding of divergent points of view, the expressions he used in his presentation were not particularly convincing for his tolerance to the kind of pluralism he advocated. The 'cardinal phenomenon of all chemistry' was the formation of electron pairs. For Lewis this was an actual pairing and not a convenient mode of explanation. He could not offer an explanation of the mechanism itself, but he had no doubt that sooner

or later quantum theory would provide an explanation of electron pairing.

In the same meeting R H Fowler stressed that the great advantage of Lewis's work was that it was model independent. The only necessary assumption was that the atoms are composed by a positive nucleus and electrons around it. He, then, systematically examined various chemical problems, and found that the Bohr theory together with the Lewis proposal about shared electron pairs could provide qualitative explanations to many questions, except to the problem of the tetrahedral symmetry for carbon. N V Sidgwick went a step further and attempted to explain why there should be a shared pair of electrons. He proposed that the orbit of each electron in the shared pair includes both nuclei. When the two electrons were in phase, then one of them was always available for holding the nuclei together.

The opening remarks in the session on organic chemistry by Sir Robert Robertson, who was the President of the Faraday Society, were of particular interest, since the organic chemists were the least 'physical' of the chemists. He noted the 'awakening of the necessity' among the chemists to take account of the findings of the physicists and the effort of certain members of the community 'to bring home to chemists that electronic conceptions are to explain much and to foretell a great deal in the domain of chemical philosophy'.

The applications of present day physical conceptions to the mechanism of chemical reaction is clearly in a transition stage and no scheme to which the term theory may properly be applied has yet been evolved: that is if we confine the term theory to that which has been proven as far as can be judged by its being in harmony with groups of facts and deductions acknowledged as cogent in quite independent connections [63].

About four years later most of the chemists had an awareness of the amazing explanatory power of the new quantum mechanics, yet it was difficult to see how this newly developing explanatory framework would be assimilated into the chemists' culture. Many chemists were apprehensive that such an assimilation would bring lasting, and not altogether welcome, changes to this culture. But for some, it was a risk worth taking. N V Sidgwick, in his influential book *The Electronic Theory of Valency*, had no inhibitions about letting the new quantum mechanics invade the realm of chemistry. He expressed an unreserved enthusiasm about the new quantum mechanics and adopted Lewis's theory for the non-polar bond. Faced with the full development of the new mechanics by Heisenberg and Schrödinger, but not with an application of the theory to a chemical problem, Sidgwick, in the very first lines of the preface to his book, attempted to clarify the methodological stumbling block that, he sensed, would be in the way of his fellow chemists:

In developing a theory of valency there are two courses open to the chemist. He may use symbols with no

definite physical connotation to express the reactivity of the atoms in a molecule, and may leave it to the subsequent progress of science to discover what realities these symbols represent: or he may adopt the concepts of atomic physics—electrons, nuclei, and orbits—and try to explain the chemical facts in terms of these. But if he takes the latter course, as is done in this book, he must accept the physical conclusions in full, and must not assign to these entities properties which the physicists have found them not to possess: he must not use the terminology of physics unless he is prepared to recognize its laws. I have endeavoured to conform to this principle, and not to lay myself open to the reproach of an eminent physicist, that 'when chemists talk about electrons they use a different language from the physicists'. I have been careful to avoid as far as possible the introduction of any physical hypotheses which are not already sanctioned by those who are best qualified to judge of them [64].

This was in 1927, just prior to the work of Heitler and London which would remove any ambivalence in the feelings of the chemists about the new quantum mechanics.

6. The Heitler–London paper: homopolar bonding is a purely quantum phenomenon

It was during the few months in Zurich in 1927 when Schrödinger was still at the ETH that Fritz London (1900–1954) together with Walter Heitler (1904–1981) managed to solve one of the outstanding problems of chemistry by using the newly proposed wave mechanical methods of Schrödinger. Fritz London had, in 1922, completed a doctorate in philosophy, having worked under the supervision of one of the prominent phenomenologists, Alexander Pfander at the University of Munich. He was planning to become a high school teacher and just before he took his matriculation examinations he decided to go to the University of Göttingen to M Born and work on physics. Born advised him to go to Sommerfeld's Institute of Theoretical Physics at the University of Munich. There he worked on his first paper in physics, calculating the intensity of band lines in spectra. The paper was published in 1925, just before the dramatic developments in quantum mechanics. Immediately he started working on transformation theory and on Weyl's theory attempting to unify gravitation and electromagnetism. In the meantime he had become Ewald's assistant at the Technical College in Stuttgart and in December 1926 he received a fellowship from the Rockefeller Foundation to go to Zurich and work with Schrödinger. It was a decision that would bring lasting changes to London's scientific agenda. He would no longer work on problems related to quantum theory and he would start to work on problems requiring the application of quantum mechanics—first to chemistry and, then, to low-temperature physics.

Walter Heitler became interested in physical chemistry while he was studying at the Technische Hochschule at Karlsruhe. There he came into contact with quantum theory and acquired a strong background in mathematics. Wishing to work in theoretical physics he first went to Berlin and then to Munich where, in 1926, he completed his doctorate with Karl Herzberg on concentrated solutions. He also received a fellowship from the Rockefeller Foundation and went to Copenhagen to work with J Bjerrum on a problem about ions in solutions. He very much wanted to work on quantum mechanics and decided to spend the rest of his time from the fellowship in Zurich with Schrödinger [65].

Heitler and London's greatest achievement was to show that the mysterious chemical binding of two *neutral* hydrogen atoms to form a hydrogen molecule could *only* be understood in terms of the principles of the new quantum mechanics. Their initial aim was to calculate the interaction of the charges of two atoms. Nothing indicates that London and Heitler were either given the problem of the hydrogen molecule by Schrödinger or that they had detailed talks with the latter while they were proceeding with their calculations. The problem of the hydrogen atom and the hydrogen molecular ion had already been solved and there was a lot of talk about the possibilities of quantum mechanics to deal with actual *chemical* problems. The simplest and deeply intriguing problem was the hydrogen molecule, whose solution would clarify the ever present question of the homopolar bond. They were not particularly encouraged by their first results, since the attraction due to the 'Coulomb integral' was too small to account for the homopolar bond between two hydrogen atoms. They realized, however, that the bonding was due to the 'exchange integral'. Its physical significance was not evident to them at first, even though Heisenberg's treatment of the helium atom, based on the quantum mechanical resonance phenomenon, had already been published.

Heitler and London started their calculations by considering two hydrogen atoms coming slowly close to each other. Electron 1 will belong to atom *a* and electron 2 to atom *b*, or electron 2 will belong to atom *a* and 1 to *b*. Because the electrons were identical, the total wavefunction of the system was the linear combination of the wavefunctions of the two cases:

$$\Psi = c_1\psi_a(1) + c_2\psi_b(2).$$

They found two values for the energy:

$$E_1 = 2E_0 + ((C + A)/(1 + S_{12}))$$

$$E_2 = 2E_0 + ((C - A)/(1 - S_{12})).$$

The integrals *C* (Coulomb integral) and *A* (exchange integral) had negative values, but *A* was larger than *C*. E_1 implied $c_1/c_2 = 1$ and E_2 implied $c_1/c_2 = -1$. Hence the wavefunction of the system could now be written as

$$\Psi_I = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)$$

$$\Psi_{II} = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1).$$

Up to now, the spin of the electrons was not taken into consideration. The symmetry properties required by the Pauli exclusion principle were satisfied only by Ψ_1 . This was the case when the electrons had antiparallel spins. But Ψ_1 corresponded to E_1 . E_1 was less than $2E_0$, the sum of the energies of the two separate hydrogen atoms, and, hence, it signified attraction. Ψ_{II} , which, when spin was taken into consideration, was a symmetric combination, corresponded to E_2 . But E_2 was greater than $2E_0$ and it implied repulsion. The ‘mechanism’ responsible for the bonding between the two neutral hydrogen atoms was the pairing of the electrons, which became possible only when the relative orientations of the spins of the electrons were antiparallel. To form an electron pair it did not suffice to have only energetically available electrons, but they had to have the right spin orientations. Exchange forces could, in principle, exist in systems without spin. Spin is crucial in the work of Heitler and London not only because it leads to an understanding of electron pairing, but also because the impossibility of forming a helium molecule is shown to be due to spin considerations. Covalent bonding was a pure quantum effect, since its explanation depended on quantum mechanical resonance and the spin of the electron, both of which have no classical analogue. ‘It is a result which by means of classical concepts can only be described very artificially’ [66].

They soon realized that the proposed exchange mechanism obliged them to confront a fundamentally new phenomenon. They had to answer questions posed by experimental physicists and chemists, like ‘What is really exchanged? Are the two electrons really exchanged? Is there any sense in asking what the frequency of exchange is?’

It became gradually clear to me that it has to be taken as a fundamentally new phenomenon that has no proper analogy in older physics. But I think the only honest answer today is that the exchange is something typical for quantum mechanics, and should not be interpreted—or should not try to interpret it—in terms of classical physics [67].

Both London and Heitler in all their early writings repeatedly stressed this ‘non-visualizability’ of the exchange mechanism—something which was clear to Bohr, Heisenberg and Pauli from the very beginning of quantum mechanics. Nevertheless, this aspect of quantum mechanics, often in the name of didactic expediency, has been consistently misrepresented.

London proceeded to a formulation of the Pauli principle for cases with more than two electrons, which was to become more convenient for his later work in group theory: the wavefunction can at most contain arguments symmetric in pairs; those electron pairs on which the wavefunction depends symmetrically have antiparallel spin. He considered spin to be the constitutive characteristic of quantum chemistry. And since two electrons with antiparallel spin were not identical, the Pauli principle did not apply to them and one was, thus, legitimized to choose the symmetric solution.

The possibility of a homopolar chemistry rests quite essentially on the fact that the electrons can still differ from each other in one respect, which we have completely ignored until now There are so to speak two different kinds of electrons, depending on the direction of their spin vectors, and as the Pauli principle is only a statement concerning absolutely identical particles, it implies no restriction at all when the spin vectors point in opposite directions [68].

With the Pauli principle it became possible to comprehend ‘valence’ saturation and, as it would be so articulately argued in the future work of both Heitler and London, spin would become one of the most significant indicators of valence behaviour and, in the words of Van Vleck, would forever be ‘at the heart of chemistry’ [69].

7. Pauling’s resonance structures

In April 1926 Linus Pauling (1901–1993), supported by a Guggenheim Fellowship, arrived in Munich where he planned to work at the Institute of Theoretical Physics. He was 25 years old and had already received his doctorate from the California Institute of Technology, having worked with Roscoe Dickinson on the structure of molybdenite. When he met Sommerfeld, the latter suggested that Pauling work on the electron spin. Pauling did not really follow this advice, since his main interest was in chemistry. When he was in Munich he discussed the problem of the chemical bond with various people and he, himself, thought it could be solved by using a Burrau-like approach (see below) and the Pauli principle. He was impressed by Condon’s treatment of the hydrogen molecule, whose clever numerology and ‘empirical method’ were congenial to Pauling, especially since Condon ‘got results as good as Heitler and London got later’ [70].

An alternative approach to the valence bond method was first attempted by Edward Condon. A few months before the appearance of the paper by Heitler and London, Condon, while he was in Munich as a Fellow of the International Educational Board, published a short paper attempting to use the new quantum mechanics for the hydrogen molecule (1927). He had received his doctorate from the University of California at Berkeley working with Birge on problems in spectroscopy and had already spent some time in Göttingen. His starting point was Øyvind Burrau’s numerical calculation of the integrals in the problem of an electron moving under the influence of two fixed centres. Condon first added the nuclear repulsive energy to the values found by Burrau. Then he dealt with the neutral hydrogen molecule where the two electrons were considered to have no mutual influence because of the Pauli principle. The final term to be considered was the mutual interaction of the two electrons. Here he made use of an important result from Hund’s (1927) analysis: the electronic term of the lowest state of a molecule changes continuously from its value for a neutral atom of equal number of electrons to

its value for the dissociated atoms. Hund's work enabled the understanding of the way a continuous transition can exist between ionic and atomic binding. In the separated atoms the molecule may be said to be latent, in that the molecular quantum numbers already exist before the atoms come together, and this was a purely quantum mechanical result. Condon used A Unsöld's (1927) calculation of the electron interaction in the unexcited helium atom to find quite a satisfactory agreement with the measured values for the heats of dissociation of the hydrogen molecule. The approximation was obviously very rough, yet it was encouraging: 'It seems proper to emphasize that Burrau's calculation of H_2^+ and the extension here to H_2 constitute the first quantum-theoretic quantitative discussion of the binding of atoms into molecules by electrons—the valence forces of chemistry. The quantitative success of the new quantum mechanics in the face of the classical theory's failure must serve to lend strong support to the new methods' [71].

After Munich and before going to Copenhagen in late 1927, Pauling spent three months in Zurich where he met Heitler and London. Right after the appearance of the Heitler–London paper, he published a short note to bring attention to an unforgivable omission: Lewis was nowhere mentioned in the paper, and Pauling was to emphasize that London's extension of the Heitler–London approach 'is in simple cases entirely equivalent to G N Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence' [72], acknowledging at the same time that the quantum mechanical explanation of valence is more powerful than the old picture. In this paper he mentioned for the first time that the changes in quantization may play a dominant role in the production of stable bonds in the chemical compounds. That was the first hint as to the hybridization of orbitals. He perceived that perturbations to the quantized electronic levels may produce directed atomic orbitals whose overlapping would be better suited for the study of chemical bonds. Pauling also suggested the direction along which he would move to derive some new results and he explicitly stated his methodological commitments. When Pauling informed Lewis about his short note [73], Lewis's response contains what is, perhaps, his most insightful statement about valence.

I was very much interested in your paper as I had been in London's, and there is much in both papers with which I can agree... I am sorry that in one regard my idea of valence has never been fully accepted. It was an essential part of my original theory that the two electrons in a bond completely lose their identity and can not be traced back to the particular atom or atoms from which they have come; furthermore that this pair of electrons is the only thing which we are justified in calling a bond. Failure to recognize this principle is responsible for much of the confusion prevailing in England on this subject, where they still talk of polar bonds and semi-polar bonds, and so on. I think in London's paper and

in yours a little too much emphasis is placed upon the origin of the paired electrons [74].

Pauling felt more at ease with the Schrödinger approach rather than with matrix mechanics and did not worry about questions about the interpretation of quantum mechanics. 'I tend not to be interested in the more abstruse aspects of quantum mechanics. I take a sort of Bridgmanian attitude toward them.' [75]

Almost everything in the series of Pauling's papers starting in 1931 and titled *The Nature of the Chemical Bond* are included in his book of the same title. Concerning the electron-pair bond, Pauling proposed six rules. Some of these rules were not derived from first principles, but were mostly inferred from rigorous treatments of the hydrogen molecule, the helium atom and the lithium atom. Pauling exploited maximally the quantum mechanical phenomenon of resonance and was eventually in a position to formulate a comprehensive theory of chemical bonding. The success of the theory of resonance in structural chemistry consisted in devising the actual structures of various molecules as a result of resonance among other 'more basic' structures. In the same manner that the Heitler–London approach provided a quantum mechanical explanation of the Lewis electron pair mechanism, the quantum mechanical theory of resonance provided a more sound theoretical basis for the ideas of tautomerism, mesomerism and the theory of intermediate state [76].

8. Mulliken and his molecular orbitals

Although the method of molecular orbitals was first introduced by Hund, it was Robert S Mulliken (1896–1986) who provided both the most thorough treatment of the different kinds of molecules as well as the theoretical and methodological justifications for legitimizing the molecular-orbital approach. Mulliken was born in 1896 and received his doctorate from the University of Chicago in 1921, working with D W Harkins on isotope separation, especially of mercury. He had worked at the University of Chicago and at Harvard as a National Research Fellow and by 1926 he was an assistant professor at New York University. When he did his foundational work on the method of molecular orbitals he had moved to the University of Chicago and had spent some months travelling in Europe, before his extended stay there in 1930 as a Guggenheim Fellow.

After his work on band spectra and the assignment of quantum numbers to electrons in molecules, Mulliken proceeded to formulate his approach to the problem of valence in a series of papers in 1932. He was getting ready for 'an attack on the Heitler and London theory of valence', as he wrote to Birge in 1931, since he was becoming more and more convinced that 'one can understand chemical binding decidedly better and more intimately, by a consideration of molecular electron configurations than by Heitler and London's method' [77]. The theory was, in a way, the

outcome of a program whose aim was to describe and understand molecules in terms of (one-electron) orbital wavefunctions of 'distinctly molecular character'. The attempt was to articulate the autonomous character of molecules through a process that depended on analogies with atoms and the extensive data concerning band spectra. In fact, his theory became an alternative mode to the treatment of the problem of valence by Heitler, London, Pauling and Slater. Holding the view that the concept of valence itself is one which should not be held too sacred, Mulliken proceeded to a succinct statement of what would be known as the molecular orbital approach to chemical bonding.

Another conception, which seems to correspond in a more natural way to our knowledge of the structure of diatomic molecules based on the interpretation of their spectra, is that we must assume not only bonding and non-bonding electrons, but also anti-bonding electrons, i.e. electrons which actively oppose the union of the atoms [78].

For he adopted a 'molecular' point of view where the emphasis was on the existence of the molecule as a distinct individual and not as a union of atoms held together by valence bonds. Therefore, from such a 'molecular' point of view the understanding of the mechanism of uniting atoms became of secondary importance.

Unshared electrons were described in terms of atomic orbitals and the notion of molecular orbitals was introduced to describe shared electrons. Electrons were divided into three categories according to their roles in the binding process: shared electrons (at least for diatomic molecules) were either bonding or anti-bonding electrons, and unshared electrons were non-bonding electrons. The latter occurred in diatomic molecules only when accompanied by a larger number of bonding electrons. Furthermore, in his method molecular orbitals were conceived as 'entities quite independently of atomic orbital' [79].

Mulliken urged the distinction between Heitler and London's valence theory and their 'valuable perturbation-method for calculating energies' of molecule formation. He thought that the theories of Heitler and London, Pauling and Slater might be called *electron-pairing* theories, whereas Lewis's theory was an *electron-pair* theory [80]. Mulliken time and again emphasized that the concept of the bonding molecular orbitals was more general, more flexible and certainly more 'natural' than the Heitler-London electron-pair bonding—even though the latter might turn out to be more convenient for obtaining quantitative results for a number of problems.

The assignment of the various quantum numbers to the molecular orbitals led to an alternative explanation of homopolar valence that did not depend on resonance, but rather on a new notion, that of promotion, introduced by Mulliken. Bonding-electrons became, in effect, unpromoted electrons, whereas antibonding electrons were represented as strongly promoted electrons.

Therefore, chemical combination of the homopolar type was the result of the shrinkage and consequent energy decrease of atomic orbitals in the fields of the neighbouring nuclei, when such orbitals were shared with little or no promotion. It was also shown that the role of the exchange integrals of Heitler and London corresponded to the electron density of the molecular orbitals: bonding orbitals had a higher electron density, antibonding orbitals had a lower density in the region between the nuclei than the densities that would have resulted from the overlapping of the electron densities of the orbitals of isolated atoms. Mulliken placed himself in the antipodes of Heitler and London. He insisted that the occurrence of electron pairs in the molecules had 'no fundamental connection with the existence of chemical binding' [81]. The Pauli principle could adequately explain the fact that each type of molecular orbit can be occupied by just two electrons.

In a paper titled 'On the method of molecular orbitals', published in 1935, Mulliken expressed his views on what he considered to be the most characteristic and differentiating aspects of his theory. The Heitler-London method 'follows the ideology of chemistry and treats every molecule, so far as possible, as composed of definite atoms... It has had the notable success as a qualitative conceptual scheme for interpreting and explaining empirical rules of valence and in semiquantitative, mostly semiempirical calculations of energies of formation' [82]. His method of molecular orbitals departed from 'chemical ideology... and treats each molecule, so far as possible, as a unit'. This seemingly terminological difference highlighted the more theoretical issues involved in the study of molecular physics.

It is the writer's belief that, of the various possible methods, the present one may be the best adapted to the construction of an exploratory *conceptual scheme* within whose framework may be fitted both chemical data and data on electron levels from electron spectra. A procedure adapted to a broad survey and interpretation of observed relations is here aimed at, rather than (at first) one for quantitative calculation, which logically would follow later [83].

Mulliken had realized that one of the reasons for the poor quantitative agreement using the molecular orbital approach was because of the inability of this theory to include the details of the interactions between electrons. But even though their inclusion would make a theoretical calculation from first principles an impossible job, 'their qualitative inclusion has always formed a vital part of the method of molecular orbitals used as a *conceptual scheme* for the interpretation of empirical data on electronic states of molecules' [84]. Such considerations, in fact, led to the qualitative explanation of the paramagnetism of oxygen—one of the main weaknesses of the valence bond approach.

Epilogue

Too often many of the theoretical successes in chemistry are regarded as developments which bring chemistry nearer to physics and that they almost always owe their legitimacy because of their closeness to the culture of physics. In examining the ways chemists attempted to deal theoretically with the classic problems of chemistry, the historian is invariably confronted with the chemists' particular attitude on how much one could and should 'borrow' from physics in order to construct a chemical theory and what is the methodological status of empirical observations for theory building in chemistry. The choices of the chemists and the schemata they proposed brought into being new research traditions, articulated new strategies of experimental manipulation, implied a different role for mathematics in each tradition, and gave rise to different styles of research within these traditions. It is the confluence of all these processes that eventually became decisive in forming the chemists' culture.

At a conference in 1977 commemorating half a century of valence theory, Charles Alfred Coulson gave the closing talk. He was a mathematician by training and a writer of what became one of the standard textbooks on valence. He claimed that the 50 years of valence theory meant 50 years of changing ideas about the chemical bond. He divided this period into three parts. He put great emphasis on the first third of the period when chemists were concerned with identifying the electronic nature of the bond, and in 'escaping from the thought forms of the physicist'.

It appears that one of the most radical ways chemists devised for 'escaping the thought forms of the physicists' was their understanding of 'how electrons spent their leisure time'.

Acknowledgment

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- [38] See Kragh, *Bohr's Atomic Theory and the Chemists* pp 474–7
- [39] Lewis [33], p 772 Lewis did not elaborate further the inadequacy of Rutherford's model vis-a-vis chemical phenomena. Several years later he was more specific: If the electrons are to be regarded as taking an essential part in the process of binding atom to atom in the molecule, it seemed impossible that they could be actuated by the simple laws of force, and travelling in the orbits, required by the planetary theory. The permanence of atomic arrangements . . . is one of the most striking of chemical phenomena. . . . It appears inconceivable that these permanent . . . configurations could result from the simple law of force embodied in Coulomb's law'. Lewis, *Valence*, pp 55–6
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- [61] Cf Langmuir's remark that 'Lewis's treatment of this subject was rather brief and perhaps for this reason it does not seem to have met with the general acceptance which it deserves'. Langmuir I 1919 The arrangement of electrons in atoms and molecules *J. Am. Chem. Soc.* **XLI**(6); in his *Collected Papers* **6** pp 9–73, on p 27. See also Kohler, 'Irving Langmuir', p 57 and Russell, *The History of Valency*, p 285
- [62] Thomson J J 1923 *Proc. Faraday Soc.* p 450
- [63] *Ibid* p 483
- [64] Sidgwick N F 1927 *The Electronic Theory of Valency* (Cambridge: Cambridge University Press) p ii
- [65] For details see Gavroglu K 1995 *Fritz London, A Scientific Biography* (Cambridge: Cambridge University Press)
- [66] Heitler W and London F 1927 Wechselswirkung neutraler Atome und homoopolaren Bindung nach Quantenmechanik *Z. Phys.* **44** 455–472, on p 456
- [67] Interview with Walter Heitler by John Heilbron (March 28, 1963). Archive for the History of Quantum Physics, American Institute of Physics.
- [68] London F 1928 Quantenmechanik und chemische Bindung *Quantentheorie und Chemie* (Hirzel) pp 59–84, on p 63
- [69] Van Vleck J 1970 Spin the great indicator of valence behaviour *Pure Appl. Chem.* **24** 235–255, on p 240
- [70] Interview with Linus Pauling by John Heilbron (March 27, 1964). Archive for the History of Quantum Physics, American Institute of Physics, p 8.
- [71] Condon E U 1927 Wave mechanics and the normal state of the hydrogen molecule *Proc. Nat. Acad. Sci.* **13** 466–470, on p 470
- [72] Pauling L 1928 The shared electron chemical bond *Proc. Nat. Acad. Sci.* **14** 359. Heitler and London had mentioned only Kossel's work.
- [73] L Pauling to G N Lewis March 7, 1928, Lewis Archives, College of Chemistry, University of

California at Berkeley. 'It pleases me very much that in the new atomic model the salient features of the Lewis atom have been reproduced as much as those of the Bohr atom'.

- [74] G N Lewis to L Pauling, May 1, 1928
- [75] Pauling interview, p 9
- [76] These theories considered it possible for the actual state of a molecule to differ from that represented by any single classical valence-bond structure, and to be intermediate between those represented by two or more valence bond structures. The quantum mechanical resonance approach led to an understanding of the conditions under which a molecule can be expected to exist in an intermediate stage or mesomeric state, as well as an accounting for the greater stability of those molecules that are the result of resonance.
- [77] Mulliken to Birge, March 26, 1931, The Bancroft Library, Birge Correspondence, Box 32, Folder 1929-1948
- [78] Mulliken R S 1932 Bonding power of electrons and theory of valence *Chem. Rev.* **9** pp 347-88, on p 349
- [79] Mulliken R S 1932 Electronic structure of polyatomic molecules and valence. II. General considerations *Phys. Rev.* **41** 49-71, on p 51
- [80] *Ibid* pp 54-5
- [81] *Ibid* p 56
- [82] Mulliken R S 1935 Electronic structures of polyatomic molecules and valence. VI. On the method of molecular orbitals *J. Chem. Phys.* **3** 375-8, on p 376
- [83] *Ibid* p 375
- [84] *Ibid* p 378