

# From Physical Chemistry to Quantum Chemistry: How Chemists Dealt with Mathematics

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**Abstract:** Discussing the relationship of mathematics to chemistry is closely related to the emergence of physical chemistry and of quantum chemistry. We argue that, perhaps, the most significant issue that the ‘mathematization of chemistry’ has historically raised is not so much methodological, as it is philosophical: the discussion over the ontological status of theoretical entities which were introduced in the process. A systematic study of such an approach to the mathematization of chemistry may, perhaps, contribute to the realist/antirealist debate. To this end, in this paper we briefly discuss Lewis’ introduction of fugacity and activity to his chemical thermodynamics and more fully analyze the issues surrounding the appropriation of resonance by Linus Pauling into quantum chemistry, particularly as these issues arose in organic chemistry as discussed by George W. Wheland.

**Keywords:** *mathematization of chemistry, theoretical entities, ontological status, physical chemistry, chemical thermodynamics, quantum chemistry.*

## 1. Introduction

As it happens with all scientific disciplines, the history of chemistry is also the history of its shifting relations with other disciplines, more specifically physics and mathematics. In what concerns mathematics and chemistry, there have been impressively divergent views. August Comte in his *Cours de Philosophie Positive* (1830-42) claimed that “all attempts to bring chemical questions into the domain of mathematics must be regarded as profoundly irrational, and antipathetic to the nature of these phenomena” (quoted in Coulson 1974, p. 8). A century later, the theoretical chemist H.C. Longuet-Higgins wrote a paper titled ‘An application of chemistry to mathematics’ in which an empirical generalization in organic chemistry suggested a theorem of some intrinsic mathematical interest (Longuet-Higgins 1953, p. 99).

What happened during these hundred years? Had the nature of chemical phenomena, which, according to Comte, repelled any thoughts about using mathematics in chemistry, changed? Was this a century during which chemistry, in effect, became a branch of physics? Was it the case that new mathematical descriptions of chemical entities and methods were, in the meantime, developed and appeared to be much more amenable to chemistry than the previous mathematical apparatus? Or, has it been the case that chemistry became a ‘proper’ science with its own full blown theoretical framework which, of course, needed the necessary mathematics for its further development? The quick answer to all these questions is to say yes and no, and in what follows we shall try to provide some cases where this ambivalent attitude in answering such questions becomes more pronounced.

By the end of the 18<sup>th</sup> century five (empirical) laws expressed the wealth of chemical observations gathered over many decades. The atomic hypothesis of 1804 ‘explained’ these laws, and chemistry – the empirical science *par excellence* – appeared to begin to have some kind of theory, expressed through some rather primitive mathematical terms. At the beginning of the 19<sup>th</sup> century, the mathematics of chemistry was not as rigorous and *a priori* as that associated with natural philosophy, but, nevertheless, chemistry could boast an equal share of success despite the fact that such progress was not really dependent on mathematics. Everyone was convinced that natural philosophy and chemistry would follow their separate and distinct paths. It was, also, deemed that the use of mathematics was by no means a prerequisite neither for further consolidating the prestige of chemistry nor for guaranteeing its further progress. Mathematics appeared not to be the chemists’ cup of tea.

Surely no one suspected what was in store for chemistry. Mathematics, which within the chemists’ culture was neither a friend nor a foe of the chemists, had, by the beginning of the 20<sup>th</sup> century, and in the words of the British chemist Arthur Smithells, brutally invaded the realm of chemists (British Association for the Advancement of Science 1907, p. 394). In the meantime, thermodynamics, one of the most successful theories of all time, which came to be part of physics, started, with some modifications, to provide a theory for chemistry as well, and in the hands of Wilhelm Ostwald, Jacobus van’t Hoff, J.D. van der Waals, and G.N. Lewis chemical thermodynamics reached levels of unsurpassed sophistication. But such developments were not particularly welcomed by the rank and file. The threat was not only because of the new language. By the end of the century the atom, the chemists’ ‘very own’ entity, was appropriated by physicists, who were, thus, threatening to turn chemistry into one of their subspecialties. Horror swept the ranks of many chemists when they realized that there were, indeed, chemists, who, as willing accomplices, viewed such developments as imperative for the progress of chemistry.

Part of the difficulty in assessing the role of mathematics in chemistry is that such a relationship is almost always mediated by physics: the two dramatic instances of the mathematization of chemistry – physical chemistry and quantum chemistry – depended heavily on two theories of physics – thermodynamics and quantum mechanics. As a consequence, mathematics has been taken repeatedly as the language in which physical theories are expressed, and, by implication, as a language also important for articulating results in theoretical chemistry. Though this is certainly true, it is not the whole truth. A philosophically inclined theoretical and quantum chemist, such as Charles Alfred Coulson, has pointed to the qualitatively different roles played by mathematics in physical chemistry and in quantum chemistry. He claimed that it was not algebra, but the mathematics behind quantum mechanics, that is, the exploration of mathematical methods to find approximate solutions of a very special differential equation – known as Schrödinger's equation – which enabled mathematics to alter substantially our understanding of chemistry (Coulson 1974).

In this paper, we explore two different instances of the issues raised by the use of mathematics in chemistry. We take two examples from the history of chemistry to show the intricate ways ontological issues came to surface as a result of the mathematization of chemistry. We briefly discuss Lewis' introduction of fugacity and activity to his chemical thermodynamics and more fully analyze the issues surrounding the appropriation of resonance by Linus Pauling into quantum chemistry, particularly as these issues arose in organic chemistry as discussed by George W. Wheland. Elsewhere, we have discussed how physical chemistry and quantum chemistry were central to understand the role of theory in chemistry and the theoretical particularity of chemistry (Gavroglu & Simões 2012). Here we argue that in addition to the host of methodological issues that the discussion of the relationship of chemistry and mathematics brings out, there is very often an ensuing issue which is the ontological status of the theoretical entities which are articulated through the use of mathematics in chemistry. Concerning Lewis and Pauling, apart from discussing the ways they adopted and adapted mathematics into chemistry, the specific concepts or theoretical entities they articulated gave rise to questions that scrutinize the ontological status of these entities: What 'exactly' are fugacity, activity, and resonance (or, exchange energy, in the case of Heitler and London)? How directly can all these be observed? Are measurements related directly to a material characteristic of the chemical reactions involved? Or are these entities devised only for providing a convenient framework for calculating a number of parameters?

The use by chemists of analogies with various concepts of physics has been amply pointed out by historians and philosophers of chemistry. Such analogies have predominantly been used by physical and quantum chemists

and have often been the trademark of their theoretical practice. However, it has not been sufficiently emphasized that such theoretical practice has been invariably complemented by a kind of a quasi social practice by the same chemists: their conscious efforts to devise legitimizing strategies for the outcomes of these analogies, for convincing the community of chemists that analogies with physical concepts bring about concepts that could surely be appropriated by chemists and help them delineate emerging new areas of chemistry. Neither Ostwald with his energetics nor van't Hoff with his chemical thermodynamics were content with merely developing their theoretical framework. Both developed well considered plans for approaching other chemists – be it with popular writings, public lectures, new journals, or re-publishing already published results – and tried to convince the great majority of chemists of the time who considered such schemata as incredibly complex mathematical structures with almost no relevance to everyday chemistry. Lewis' fugacity and activity were concepts brought about through analogies to the concept of entropy (or the concepts of partial pressures and concentrations). In a similar manner, Pauling proceeded to develop his resonance theory of the chemical bond, through analogies with Heisenberg's idea of resonance and Heitler and London's concept of the exchange effect. Rather than viewing the results of such analogies as the long hand of physics threatening the autonomy of chemistry, both Lewis and Pauling introduced these new concepts and developed the relevant methods, through processes of appropriation which (further) delineated the borders of both physical chemistry and quantum chemistry. Both Lewis and Pauling tried to convince chemists that such concepts were not alien to the chemists' culture and that their adoption would delineate the newly emerging (sub)disciplines – physical chemistry in the case of Lewis and quantum chemistry in the case of Pauling – and 'make' them part of chemistry.

In both instances, the discussion of the relationship between chemistry and mathematics involved both methodological issues and ontological commitments, and we claim that behind the methodological proposals were often discussions concerning the ontological status of many (new) mathematically tractable theoretical entities (or concepts). Interestingly, in the two cases under discussion, the relationship between chemistry and mathematics appears as a relationship which has *both* a philosophical as well as a historical aspect: issues related to the realist/antirealist debate are intermingled with issues related to the historically situated strategies of legitimization of the new approaches/concepts. In what follows we attempt to bring out this dual character of the relationship: by providing some of the historical aspects we show how they gave rise to the philosophical aspects. Clearly, the systematic considerations of these philosophical issues do not comprise the aim of this paper.

The first case refers to a rather idiosyncratic program in ‘de-entropising’ chemistry. At about the same time as chemists were trying to reappropriate the atom from physicists, they were also trying to misappropriate entropy. It should be noted that the formulation of chemical thermodynamics did not automatically lead to its adoption by the chemists. There ensued a stage of adapting chemical thermodynamics to the exigencies of the chemical laboratory. Chemical thermodynamics had to appeal to the chemists not only because it would provide a theory for chemistry, but first and foremost because it would form a framework sufficiently flexible to include parameters which could be unambiguously determined in the chemical laboratory. Lewis’ idiosyncratic theoretical agenda for chemical thermodynamics played a prominent role in this process. Although deeply committed to thermodynamics, he proposed notions whose outstanding characteristic was that their determination was independent of entropy considerations. His original concepts of fugacity and activity were, in effect, definitions of free energy. He aimed at the definition of conceptual entities which could be of practical use to experimentalists but which could avoid a direct reference to entropy. Lewis made efforts to propose visualizable entities, something that was not independent of his special relations with particular laboratory practices. His successive reformulations of thermodynamics and the central role he assigned to fugacity and activity let him start, and for many years continue, an experimental program around the systematic measurements of free energies of many different substances.

The second case refers to the reconstruction of the structural theory based on the concept of resonance appropriated by Pauling from the realm of quantum mechanics, building on the notions of quantum mechanical exchange effect of Walter Heitler and Fritz London, and extended to explain and predict many chemical properties, some of which proved vital to organic chemistry. Pauling was an expert in presenting resonance theory as an essentially chemical theory in which rules, more or less justified by the mathematics of quantum mechanics, were essential to the articulation of the new theory. But despite Pauling’s wizardry in convincing chemists and in pushing forward steadily an agenda to impose resonance theory as *the* chemical theory *par excellence*, discussions by partisans and critics alike, extending over two decades, accompanied its further development.

## 2. G.N. Lewis’ Physical Chemistry

Gilbert Newton Lewis (1875-1946) is best remembered for his ingenious proposal that chemical bonding – both the ionic type as well as the mysteri-

ous homopolar type – could be explained in terms of shared electron pairs. It was a semi-empirical schema first proposed in 1913 and whose justification became possible only after the advent of quantum mechanics (Lewis 1913, 1916, 1923), and, more specifically, following the 1927 paper of Heitler and London. It would be misleading to assess Lewis' theory of valence on its merits alone. Lewis had a theoretical agenda, and his theory of valence was an integral part of that agenda. His work in chemical thermodynamics and the special theory of relativity displayed the same trends as his work on valence: an attempt to propose a theoretical framework within which phenomena can be accounted for in a more unifying manner by making use of fewer assumptions and more rigorous (mathematical) derivations.

For Lewis, thermodynamics could be assimilated in chemistry only if it became possible to work with parameters that could be unambiguously related to situations met in the laboratory, rather than seeking the extension of parameters originally defined for ideal systems to practical problems occurring in the laboratory. Thermodynamics would lose all its appeal for chemists if it remained a theory which could only be formulated in terms of parameters that chemists use but which could not be unambiguously measured in the laboratory. For example, it was notoriously difficult to determine exactly partial pressures and concentrations that were the parameters in terms of which most of the equations of chemical thermodynamics were formulated. Lewis proposed to base chemical thermodynamics on the notion of *escaping tendency* or *fugacity*, which he considered to be closer to the chemists' culture, more fundamental than partial pressure and concentration, and exactly measurable. He hoped that his new concept would become the expression for the tendency of a substance to go from one chemical phase to another.

If any phase containing a given molecular species is brought in contact with any other phase not containing that species, a certain quantity will pass from the first phase to the second. Every molecular species may be considered, therefore, to have a tendency to escape from the phase in which it is. [...] The quantity which we shall choose [to express this tendency quantitatively for a particular state] is one which seems at first sight more abstruse [than thermodynamic potential, vapour pressure, solubility in water], but is in fact simpler, more general and easier to manipulate. It will be called fugacity. Obviously, the fugacity of a system which is less stable is greater than that of another system which is more stable. [Lewis 1901-02, p. 54]

After discussing fugacity whose experimental determination involved difficult measurements of osmotic pressures, Lewis proposed to reformulate chemical thermodynamics in terms of the *activity* of a substance which was its fugacity divided by the product of the gas constant and the absolute temperature. The activity of a species was, according to Lewis, the "perfect measure of the tendency of a species to take part in any chemical reaction" (Lewis

1907, p. 284). Even though Lewis admitted that absolute activities of ions in a solution could not be determined, he offered a method whereby it could become possible to determine the ratio of the activities of a substance at two different concentrations, and this quantity was quite sufficient for most of the tasks confronted by the chemists. He then showed how activities were related to changes in the free-energy in reactions as well as to the electromotive force of the galvanic cells.

In 1907, Lewis published a paper titled ‘Outline of a new system of Thermodynamic Chemistry’ (Lewis 1907). From a methodological point of view, it is his most significant paper. Among other things, he explicitly articulated here his overall approach to chemical thermodynamics. He started by stating that there are, basically, two approaches in thermodynamics. The first makes use of entropy and the thermodynamic potential, which had been employed by Josiah Willard Gibbs, Pierre Duhem, and Max Planck, and the second, where the cyclic process was applied to a series of problems, had been used by van’t Hoff, Ostwald, Walter Nernst, and Svante Arrhenius. The first method dealt with ideal systems, was rigorous and exact, and had been, mainly, used by physicists, whereas chemists preferred the second. According to Lewis, the main reason for the chemists’ preference was the difference between the physicists’ notion of equilibrium and that of physical chemists.

Lewis further criticized the first method for its application “has been unsystematic and often inexact, and has produced a large number of disconnected equations, largely of an approximate character” (Lewis 1907, p. 259). And the reason for this was that nearly all of the equations had been based on the assumption that it was possible to treat the vapor of a substance as a perfect gas, or a solution as a perfect solution – one that obeyed the laws of an infinitely dilute solution. These assumptions presupposed a kind of continuity from the case of an ideal gas to a real one and, hence, explored the possibilities of a corresponding behavior. The laws derived from such assumptions were, then, *intrinsically* approximate laws. Hence, Lewis wanted to investigate the implications of the deviations found from the predictions of these laws. One expects that Lewis, whose knowledge of mathematics was quite impressive, would have attempted to apply the more exact methods of the physicists. Instead, after rejecting that approach, he developed the methods already in use among physical chemists “in such a way as to render them exact. [...] The aim is to develop by familiar methods a systematic set of thermodynamic equations entirely similar in form to those which are now in use, but rigorously exact” (Lewis 1907, p. 260). Therefore, Lewis wanted to present chemical thermodynamics in *both* a more rigorous way *and* in one that was more accessible (and therefore useful) to chemists.

Determining activities by measuring free energies was particularly convenient for chemists. It was possible to construct a table with the affinities of

a particular substance and a large number of its chemical reactions by measuring the free energy of the formation of a substance from its elements. In this way activity became a crucial quantity in Lewis' thermodynamics. The use of activities made chemical thermodynamics relevant to non-ideal systems. This new quantity allowed chemists to be able to transform the free energy values obtained when one of the constituents of a reaction was in a non-ideal state into corresponding values when all the constituents were in standard states. The standard state was the state of a substance with the activity coefficient being equal to one. To perform any conversions it was only necessary to measure the activities of substances in their non-standard states. "The problem of converting free energies of various states into free energies in standard states is the problem of determining the activities of the various substances concerned" (Lewis & Randall 1923, p. 291).

Arthur Amos Noyes, the Director of the Research Laboratory of Physical Chemistry at M.I.T., was convinced of the immense usefulness of such a compilation of free energy changes. It was a complex task, and in 1905-1906 he tried to involve several laboratories in the measurement of free energies of formation. Failing to secure such collaboration, Noyes decided that the measurements would be done at M.I.T. and Lewis took charge of the program. By the time Lewis left for Berkeley, in 1912, exact values of free energies were determined for many substances and there were impressive improvements in the experimental techniques. As Servos so aptly observed:

Lewis' concept of activity, invented as part of a personal quest to reform chemical thermodynamics, ended up being a useful tool both in the study of the anomaly of strong electrolytes and in the calculation of free energy values. Lewis' original idea, that the concepts of fugacity and activity might play a central role in the formal structure of thermodynamics, never caught on, but by 1920 physical chemists everywhere were beginning to use activities and activity coefficients in their calculations. That activities and activity coefficients became part of the vocabulary of physical chemistry was due in large part to the support given to Lewis and his ideas by Noyes and his associates at M.I.T. [Servos 1990, p. 149]

Though there was no explicit philosophical agenda in Lewis' pursuit of his 'de-entropised' thermodynamics and, indeed, his brand of physical chemistry, it is clearly the case that the methodology devised to circumvent the pitfalls of entropy in chemistry by introducing new concepts and measurable quantities, carried with it some heavy philosophical bags – predominantly among them the question as to the ontological status of the theoretical entities. His own worry was to emphasize the convenience of that way of circumventing entropy. But to the extent that entropy had brought in all kinds of conceptual complications, the introduction of these entities would be also caught up in



the vortexes of such complications, which were, in effect, of a philosophical character.

### 3. Linus Pauling: from exploring different possibilities for a quantum mechanical theory of valence to the nature of the chemical bond

Linus Pauling (1901-1994) made the most out of Lewis' notion of shared electron bonds, first in the framework of the old quantum theory, then by accommodating it in the context of quantum mechanics. He originally worked on the effect of electric and magnetic fields on the dielectric constant of hydrogen chloride and compared the results obtained by the use of the old quantum theory to those obtained by the use of the new mechanics and proved that the latter gave values of the dielectric constants in good agreement with experiment (Pauling 1926a, 1926b). It was this result, more than anything else, which convinced Pauling that quantum mechanics was necessary for the solution of chemical problems. He wrote to Noyes announcing: "I am now working on the new quantum mechanics, for I think that atomic and *molecular chemistry* will require it. I am hoping to learn something regarding the distribution of electron-orbits in atoms and molecules."<sup>1</sup>

Pauling's notebooks are especially helpful in tracing some of his early thoughts about the nature of the chemical bond (Gavroglu & Simões 1994).<sup>2</sup> The first set of notes date from 1926. In order to study diatomic molecules of identical atoms, Pauling tried to determine the form of molecular (binuclear) orbitals in the case where the internuclear potential was approximated by two identical unidimensional square-well potentials. He then integrated Schrödinger's wave equation for the electron in the different regions associated with this simplified potential. He used the boundary conditions to determine some of the constants of integration and analyzed the extremes corresponding to separated atoms at infinite distance and united atom with zero distance. The eigenfunctions obtained were either symmetrical or antisymmetrical in the position coordinate, which meant that there existed either symmetrical or antisymmetrical electron orbits. He also hinted at the role of the spinning electron in bond formation, and jotted that "the spinning electron accounts for electron pairs". Furthermore, he referred to resonance energy: "There is, of course, a continual interchange of energy among the various electrons, so that one electron cannot be assigned to a given state; and there is the corresponding resonance effect on the energy of the system."<sup>3</sup> Finally, he tried to extend his square-well potential model to the analysis of

the case of a diatomic molecule composed of two different atoms, and of polyatomic molecules composed of two large and two small atoms.

Pauling tried to develop an alternative method to that of Heitler and London, and in doing so he used the idea of resonance and the Pauli principle, which he later classified as the two fundamental aspects of chemical valence (Pauling 1928). Besides working on the interaction between two hydrogen atoms, he treated the interaction between two helium atoms, but stumbled upon some integrals for which he could not find good approximate values. But he persevered as he was convinced that “if I worked in this field I probably would find something, make some discovery, and that the probability was high enough to justify my working in the field. Of course, it led to hybridization and all of this stuff”.<sup>4</sup>

It took about three years, from the initial musings over the microscopic interpretation of the chemical bond, for Pauling to understand how to appropriate and develop the concept of exchange effect of Heitler and London (Heitler & London 1927), by extending Werner Heisenberg’s idea of resonance used to account for the properties of the helium atom (Heisenberg 1926). At the same time, Pauling felt free to interpret their paper as providing the quantum mechanical justification for Lewis’ chemical and empirical theory of the electron-pair bond (Gavroglu & Simões 1994). Besides, while studying one of London’s papers (London 1928) Pauling hit upon the idea of changed quantization, which he later called ‘hybridization’, to explain the tetravalency of carbon, the atom which plays a vital role in organic chemistry.<sup>5</sup> Certain of the novelty of his ideas and the importance of convincing chemists of their usefulness, Pauling presented his fully developed theory in a series of seven papers on ‘The nature of the chemical bond’ spanning a three-year period (Pauling 1931, 1931a, 1932a, 1932b; Pauling & Sherman 1933a, 1933b; Pauling & Wheland 1933).

In the formation of an electron-pair bond, the resonance phenomenon of quantum mechanics accounted for the energy of the covalent bond. Resonance occurred with like or unlike atoms as a result of the indistinguishability of electrons (Pauling 1931). The same resonance phenomenon was responsible for the formation of the one-electron and the three-electron bond (Pauling 1931a). Furthermore, the development of quantum mechanics facilitated the understanding of the structure of benzene ( $C_6H_6$ ) and other aromatic compounds for which no single structural formula was consistent with the observed properties that could be assigned to them. This had been a constant source of annoyance to organic chemists, and some provisional explanations had already been put forward.

In the theory of intermediate states, F.G. Arndt suggested that if two different formulae could be assigned to an organic compound, then the molecule was not in either of the states associated with each of the valence-bond

structures but was instead in a new ‘intermediate’ state involving both classical formulations. C.K. Ingold’s theory of mesomerism assumed that the actual structure of the molecules was ‘in between’ those described by the different valence-bond formulas (Nye 1993, p. 206). The new word ‘mesomerism’ was put forward to emphasize that this phenomenon was quite different from the classical phenomenon of tautomerism in which two isomers did indeed change into each other. Tautomeric molecules existed in two or more different forms, whereas in the new situation there was just one type of molecule.

In the fifth paper of the mentioned series, the inauguration of Pauling’s close association with Wheland whose future work would be decisive in the further establishment of the theory of resonance, an alternative method to study the benzene molecule was suggested. They used perturbation theory to calculate the wave function representing the normal state of the benzene molecule and to find an expression for its resonance energy. They assumed that the wave function could be written as a linear combination of five wave functions which represented the five independent canonical structures contributing to the normal state of the molecule. The principal contributions were made by the two Kekulé structures, and the rest by the three different forms assumed by the Dewar structure. But it was clear that “in a sense all structures based on a plane hexagonal arrangement of the atoms – Kekulé, Dewar, Claus, *etc.* – play a part, with the Kekulé structures most important. It is the resonance among these structures which imparts to the molecule its peculiar aromatic properties” (Pauling & Wheland 1933, p. 365). The extra energy of the molecule due to resonance among the five canonical structures was calculated as a function of the exchange integrals involving adjacent atoms. To find a numerical value for the exchange integral Pauling and Wheland used the empirical values obtained by thermochemical methods for the resonance energy of the benzene molecule (*ibid.*). In this way they were able to calculate the percentages of the total resonance energy contributed by the two groups – Kekulé and Dewar – of independent structures.

By 1935 Pauling felt that he had acquired a full understanding of the nature of the chemical bond. Always eager to have his contributions recognized quickly among his peers, Pauling used all communication channels in order to reach as many people as possible. The *Introduction to Quantum Mechanics with Applications to Chemistry* (Pauling & Wilson 1935), jointly written with E.B. Wilson, was addressed to chemists, experimental physicists, and beginning students of theoretical physics, and did not presuppose much mathematical background on the part of its readers. The book became popular even among those for whom quantum theory was not unknown territory.

During his appointment as George Fisher Baker Non-resident Professor of Chemistry at Cornell University in the fall semester of 1937, Pauling reorganized all his published papers and unpublished notes on the chemical bond

for publication in a textbook. *The Nature of the Chemical Bond* appeared in 1939 and sold so well that another edition came out in the following year. It was dedicated to Lewis, who was overjoyed by the fact.

The reasons for the popularity and persuasiveness of Pauling's classic *The Nature of the Chemical Bond* are quite complex and are not independent of the expressed assertiveness of physical chemistry in the United States, the rather articulate expression of American pragmatism and operationalism in Pauling's work as well as the deadlock of the program of analytical calculations started by Heitler and London and continued by others.

Pauling was aware of the difficulties chemists faced in understanding such unfamiliar concepts as quantum mechanical resonance and the resonance of molecules among several valence bond structures (Gavroglu & Simões 2000; Mosini 1999, 2000; Nye 2000a; Park 1999, 2005). He noted an 'element of arbitrariness' in the use of resonance because of the choice of canonical structures in discussing the state of the system, but he argued forcefully that "the convenience and usefulness of the concept of resonance in the discussion of chemical problems are so as to make the disadvantage of the element of arbitrariness of little significance" (Pauling 1939, p. 12). This, as he repeatedly stated, was his constructive criterion for theory building in chemistry. Besides, he reminded his readers that an equivalent element of arbitrariness occurred in essentially the same way in the classical resonance phenomenon.

He contrasted resonance with traditional chemical concepts such as mesomerism and tautomerism and discussed the reality of canonical structures. Even such a clear and succinct writer as Pauling could not avoid making apparently contradictory statements. As to the relation between resonance and tautomerism, Pauling seemed to be claiming at times that they were the same: "There is no sharp distinction which can be made between tautomerism and resonance." (Pauling 1939, p. 404) Elsewhere he claimed that they were distinct: "It is convenient in practice to make a distinction between the two which is applicable to all except the border-line cases" (*ibid.*), differing in the following way: "Whereas a tautomeric substance is a mixture of two types of molecules, differing in configuration, in general the molecules of a substance showing electronic resonance are all alike in configuration and structure" (*ibid.*, p. 407). The same ambiguity arose in discussing the reality of different canonical structures. Are the two Kekulé structures associated with the benzene molecule real? Pauling claimed that "there is one sense in which this question may be answered in the affirmative," but immediately added that "the answer is definitely negative if the usual chemical significance is attributed to the structures. A substance showing resonance between two or more valence-bond structures does not contain molecules with the configurations and properties usually associated with these structures" (*ibid.*, p. 408). Hav-

ing these linguistic ambiguities in mind one cannot but wonder about their repercussion in the subsequent arguments over the significance of resonance.

Pauling deemed the topic so important that he made his position public in *Perspectives in Organic Chemistry* (Pauling 1956), and later on, in the third edition of *The Nature of the Chemical Bond* (Pauling 1960). More than the question of the artificiality of the resonance concept, to which he alluded briefly in his 1954 Nobel lecture (Pauling 1954), he wanted, once and for all, to state as clearly as possible his views on theory building. In the preface to the last edition of 1960, Pauling pointed out that the theory of resonance involves “the same amounts of idealization and arbitrariness as the classical valence-bond theory” (Pauling 1960, p. vii). A whole section was added to discuss this question bearing the revealing title ‘The Nature of the Theory of Resonance’. There, he argued that the objection concerning the artificiality of the concepts applied equally to resonance theory as to classical structural theory. To abandon the resonance theory was tantamount to abandoning the classical structural theory of organic chemistry. According to Pauling, chemists should keep both theories because they were chemical theories and as such possessed basically an empirical (inductive) basis.

Disagreements on the meaning of resonance were at the center of reactions to Pauling’s proposal, and were made public even before the publication of *The Nature of the Chemical Bond*. While some were voiced by collaborators, most were put forward by opponents or critics. Determined to address organic chemists, Erich Hückel wrote a review article in 1937 criticizing Pauling’s resonance. The crux of his criticism was that the concept of resonance as articulated by Pauling suffered from an unjustifiable analogy between mechanics and quantum theory. According to Hückel, the Kekulé structures Pauling started with could be considered as a “formal analogy to two swinging pendula that are uncoupled and have the same frequency”; but this was thoroughly misplaced, because both structures exist simultaneously, neither one has a specific energy, and, thus, no frequency, which is similar to coupled pendula (Hückel 1937a, 1937b)

In fact, Hückel (1937a, pp. 764, 767) thought that the very term ‘resonance’ was misleading, and had to be dispensed with, preferring, instead, the term ‘mesomerism’ which, he thought, represented in a better way the ensuing molecular state as something in between the initial fictitious states that corresponded to canonical structures. Pauling, of course, in *The Nature of the Chemical Bond* advanced the argument that the new state was not something in between, but a completely different state which had come to be realized as a result of resonance. But Hückel was still unconvinced twenty years later (Hückel 1957), even after Pauling had, through an ingenious rhetorical strategy made ‘his’ resonance a household name in the chemical community. He repeated what he considered as crucial arguments against the use of the term

'resonance'. In his opinion, Hückel wrote, what was basically involved was not a process in which 'resonance' arose between different 'structures' as in classical physics, but merely "an analogy with a mathematical calculation procedure – a purely mathematical formalism" (*ibid.*, pp. 872-3), for solving the secular problem. This must not be confused with a real physical phenomenon. He expressed his worry that many chemists attach 'inappropriate meanings' to terms like 'resonance', 'resonance energy', and 'resonance stabilization'. One of the basic reasons for such confusion was the formal mathematical analogy with classical pendula, and that resonance itself was a '*physical process*'. He insisted that it would be better to "speak of '*line diagrams*' rather than of *structures*" (*ibid.*, p. 873).

But Hückel was going against a culture of the chemical community which was formed for over a century. Visualizability had become one of the defining characteristics of the chemists' culture, and non-visualizable configuration space was alien territory. If one is to judge things, Hückel was right concerning his criticism of resonance. After all, even some advocates of resonance, such as Wheland, thought the same.

Disagreements with Hückel, and later with Wheland, on the question of the ontological status of resonance were not the only ones Pauling had to face. His theory of resonance was viciously attacked in 1951 by a group of chemists in the Soviet Union in their Report of the Commission of the Institute of Organic Chemistry of the Academy of Sciences (Kursanov et al. 1952, Tatevskii Shakhparanov 1952, Hunsberger 1954). As they themselves stressed, their main objection was methodological. They could not accept that by starting from conditions and structures which did not correspond to reality one could be led to meaningful results. Of course, they discussed analytically the work of Aleksandr M. Butlerov who in 1861 had proposed, according to their interpretation, a materialist conception of chemical structure: this was the distribution of the action of the chemical force, known as affinity, by which atoms are united into molecules. They insisted that any derived formula should express a real substance, a real situation. According to the Report, Pauling had moved along different directions. For him a chemical bond between atoms existed if the forces acting between them were such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.

#### 4. George Wheland: extending the scope of resonance theory

George W. Wheland's (1907-1972) *The Theory of Resonance and its Application to Organic Chemistry* first appeared in 1944 and it attempted to make as complete a presentation of resonance theory as it was then possible. It was a partisan textbook at a time when there was no outstanding experimental reason to choose between resonance theory and molecular orbital theory. Wheland's first lines in his preface left no doubt about what was the 'correct' approach: "the theory of resonance is the most important addition to chemical structural theory that has been made since the concept of the shared-electron bond was introduced by G.N. Lewis" (Wheland 1944, p. iii).

Wheland felt that the general acceptance of resonance theory had been delayed because there was no comprehensive account of the subject; with the book, he intended to provide such an account. He most probably tried in this way to come up with a textbook to substitute the aborted venture he had envisioned with Pauling of writing a joint textbook on *Quantum Mechanics of Organic Molecules*, in which an extended comparison of the valence bond theory and the molecular orbital theory was planned to be offered, together with a plea for resonance theory.<sup>6</sup> Wheland considered that although the most interesting applications of the theory are in organic chemistry, "its basis lies in the mathematical depths of quantum mechanics". (*Ibid.*) Its precise presentation can only be achieved by using complicated mathematical language. But being aware that such preconditions could not be expected of organic chemists and that, in general, they were not particularly welcomed by the chemists, Wheland suggested that "some sort of working compromise must be reached" (*ibid.*). His rhetoric is perhaps the most articulate expression of what – despite the talk of 'compromise' – was in store for the chemists.

Wheland clearly defined his agenda in both editions of the book, the second one published in 1955 (Wheland 1955): the adoption of the resonance viewpoint was the only way for quantum chemistry to become a part of chemistry and not remain one of the many instances in the applications of quantum mechanics. Just like Pauling, he was a master in appropriating quantum mechanics for chemistry and using it to further accentuate the autonomous status of quantum chemistry. In fact, though at the beginning he was somewhat apologetic for including a very long and technical chapter on quantum mechanics, he was also quite adamant in telling his fellow chemists that he was convinced that "an understanding of quantum mechanics cannot be acquired by any process of intellectual osmosis, but can be obtained only at the cost of a certain amount of conscious effort. Consequently, I do not

apologize for the fact that this new chapter will require much study and the frequent use of pencil and paper” (Wheland 1955, p. ix).

In his book dedicated to Pauling (Wheland 1944, 1955), Wheland argued that the resonance concept was a ‘man-made-concept’ in a more fundamental way than in most other physical theories (Gavroglu & Simões 1994, 2000; Mosini 1999, 2000; Park 1999). In the first edition of the textbook, Wheland put forward the analogy between a resonance hybrid and a mule. Such as a mule is a hybrid between a donkey and horse without oscillating between the two, such does a resonance hybrid not result from an oscillation between component valence structures, as often voiced in the literature by organic chemists. But the analogy is misleading in a very dangerous way: donkeys and horses are existing entities, and Wheland did not believe that such was the case for the component structures (Wheland 1944, p. 3).

The criticisms voiced by the Russians on ideological and nationalistic grounds prompted Wheland to refine his analogical argument in the second edition of his textbook. Now, he put forward an analogy in which the resonance hybrid was related to a rhinoceros, an exotic animal known to medieval people from hearsay, presented as a hybrid between two fictional creatures, the dragon and the unicorn, which populated the imaginary world of human beings. The rhinoceros, as well as the hybrid, is a real entity whose properties were related to those of its fictional component parts (Wheland 1955, p. 4). But this analogy could still be misleading in the sense that the hybrid could be said to share average properties between two component structures, while nothing restrained the number of component structures, nor their relative weight. To express such ideas, Wheland refined again his argument and related the properties of the resonance hybrid to the personality of a real man named John Doe who shared the characteristics of fictional characters such as Sherlock Holmes, Don Quixote, and Sir Galahad, in a certain proportion (Wheland 1955, p. 5). In any case, Wheland continued to believe that resonance was essentially a ‘man-made’ concept, as he himself named it, and was to elaborate his view very soon.

The higher degree of ‘man-madness’ of resonance immediately raised a harsh discussion in private between Wheland and Pauling, soon after the second edition of Wheland’s textbook came out. Wheland justified this statement as a way to counter the widespread view that resonance was “a real phenomenon with real physical significance,”<sup>7</sup> which he classified as one example of the nonsense organic chemists in many instances were prone to. For him, resonance was not an intrinsic property of a molecule that is described as a resonance hybrid. It was not something that the hybrid does, or that can be ‘seen’ with a sufficiently sensitive apparatus. Instead, it was something deliberately added by the chemist or physicist who talked about the molecule. It was simply a description of the way that the physicist or chemist arbitrarily



chose for the approximate specification of the true state of affairs. He went on to illustrate his viewpoint by means of the following analogy.<sup>8</sup>

In anthropomorphic terms, I might say that the molecule does not know about resonance in the same sense in which it knows about its weight, energy, size, shape, and other properties that have what I call real physical significance. Similarly [...] a hybrid molecule does not know how its total energy is divided between bond energy and resonance energy. Even the double bond in ethylene seems to me less ‘man-made’ than the resonance in benzene. The statement that the ethylene contains a double bond can be regarded as an indirect and approximate description of such real properties as interatomic distance, force constant, charge distribution, chemical reactivity, and the like; on the other hand, the statement that benzene is a hybrid of the two Kekulé structures does not describe the properties of the molecule so much as the mental processes of the person who makes the statement. Consequently, an ethylene molecule could be said to know about its double bond, whereas a benzene molecule cannot be said, with the same justification, to know about its resonance [...]

Pauling could not disagree more. For him, the double bond in ethylene was as ‘man-made’ as resonance in benzene. Pauling summarized their divergent viewpoints by saying that for Wheland there was a ‘quantitative difference’ in the ‘man-made’ character of resonance theory when compared to ordinary structure theory – a difference he could not find anywhere. He further asserted that his former student did a disservice to resonance theory by over-emphasizing its “man-made character”.<sup>9</sup> Wheland conceded that resonance theory and classical structural theory were qualitatively alike, but he still defended, contrary to Pauling, that there was a “quantitative difference” between the two.<sup>10</sup>

Despite all discussions no consensus was ever attained concerning either the ontological status of the resonance hybrid or the epistemological status of resonance theory. Differences in points of view on the status of resonance theory ranged from Pauling’s defense of resonance theory as a chemical theory which just by accident had not been arrived at before the formulation of quantum mechanics,<sup>11</sup> to its acceptance as a mere calculational method. These differences depended certainly on the ways practitioners positioned themselves vis-à-vis molecular orbital theory, the other alternative theoretical framework to deal with valence related questions. For those sympathetic to molecular orbital theory, but also for such a stubborn advocate of resonance theory as Wheland, the resonance hybrid was not certainly a real structure but just a convenient device to express molecular properties. For Wheland opting for resonance was a matter of theoretical preferences, deeply grounded on the chemist’s traditional culture, more than anything else.

Again, more than just a straightforward discussion over alternative methods to deal with valence related questions, the musings over the nature of resonance which involved many participants, from founders such as Pauling

and Hückel to advocates of resonance such as Wheland or chemists opposing resonance such as some Russians, and which were voiced in textbooks in order to reach as many chemists as possible, involved philosophical issues centered on the philosophical status of chemical concepts. The fact that there were diverging views on such philosophical issues, or that they involved primarily an elite of quantum chemists does not in any way deprive them from their fundamental role in the construction of quantum chemistry.

## Conclusion

The mathematization of chemistry has posed problems, has given way to lively debates among practitioners, and has fostered a range of varied reactions which cannot be reduced to the simplistic recognition of a traditional repudiation of mathematics by chemists. In the case studies discussed in this paper, our central protagonists were extremely knowledgeable in mathematics, often positioning themselves at the forefront of new mathematical avenues for chemistry. Therefore, their methodological choices and ontological commitments were never guided by an avoidance of mathematics or by an inability to understand the potentialities opened up by the appropriation of physical concepts into their respective fields. On the contrary, their choices have to be analyzed as an integral part of their scientific agendas. Additionally, they never shunned away from discussions which involved issues usually posed by philosophers of science such as the status and role of theories, the role of theoretical entities, their ontological status, to name some addressed in the preceding pages. While they were not certainly philosophers, their philosophical musings help clarify questions of philosophical import.

The theoretical agendas of Lewis and Pauling, both chemists by training and by heart, were delineated having in mind the exploration of methods or theoretical approaches which could become part and parcel of a *new* chemistry, be it physical or quantum chemistry. Their common allegiance to finding unifying chemical concepts, such as fugacity, activity, or resonance, as building blocks of *new* chemical theories, their emphasis on utility and convenience of use, their insistence on proposing concepts congenial to chemists' practices, present and future, and on the role of visualization in theory building, point to a consonance at theoretical issues and methodological and ontological allegiances which fostered successively the appropriation into the chemists' culture of newly emerging disciplines, such as physical chemistry and quantum chemistry, apparently so unfriendly to them.

The strongest themes in Lewis' theoretical agenda run concurrently in his papers on physical chemistry, relativity, and valence and, to a large extent,

define his methodological constraints. These themes include the unification and generalization of existing formulations, rigorous derivations of semi-empirical rules, preference for what is convenient rather than a preoccupation with what is actually true, and visualizability of the proposed mechanisms. Among his themes, the one dearest to Lewis and which dominated most of his work in physical chemistry and chemical thermodynamics, was his attempt to formulate general expressions which can account for as many phenomena as possible, and from which most of the existing empirical rules, semi-empirical relations, or, even, rigorously derived formulas can be produced. In his paper on 'The law of physico-chemical change', he claimed that his researches had been crowned with the success of finding a *single law* which was simple, exact, and general enough "to comprise in itself many laws and yet concrete enough to be immediately applicable to specific cases" (Lewis 1901-1902, p. 49). In his classic paper on valence published in 1916, he argued that his proposal about electron-pairing could now account for both kinds of bonds. The striking differences in properties between the extreme polar and the extreme nonpolar types with respect to which "fundamental distinctions have been made between the two types, and which seem so unconnected, are in fact closely related, and the differences are all due to a *single cause*" (Lewis 1916, pp. 763-4). And in 1930, in one of his most speculative papers, he declared that he "decided to present certain ideas" which would solve one of the outstanding problems of quantum mechanics by showing that almost all the rules which stipulated the exclusion of certain quantum states can be proved to be "direct mathematical consequences of quantum mechanics" (Lewis 1930, p. 1144). And when Joseph Mayer wrote to Lewis that he looked forward to reading his new paper concerning the foundations of thermodynamics about which he had heard enthusiastic comments from Robert Oppenheimer, Lewis, in answering, did not seem to be feeling a strong urge of humility towards his former collaborator: "My paper on thermodynamics in which I derived classical thermodynamics, as well as the whole theory of fluctuations, *from a single extremely simple assumption*, is much more fundamental than Gibbs' 'Statistical Mechanics' and its successors."<sup>12</sup>

Pauling proceeded to a rather ingenious use of a quantum mechanical notion, that of resonance, formulating another approach and a new 'theory of valence', a most idiosyncratic theory that became close to the heart of chemists, also as a result of the incessant efforts of its inventor, a most able propagandist. Neither the methodology nor the relatively intricate mathematics were part of the chemists' culture. But if one is allowed to talk in terms of a reformation of a community's culture, it is Pauling's theory which brought about deep changes, by convincing chemists that mathematics will have to be part of their culture. He talked directly to chemists, and he would not be

bothered by any objections by physicists. He kept on repeating that what he did was in the same spirit as structural theory. He asked chemists to develop a 'sense for theory'. And he claimed that what he was doing was, in effect, the theoretical justification of what Lewis, the doyen of American chemists, had already suggested so successfully nearly twenty years earlier: an explanation of the otherwise mysterious electron pair mechanism. Pauling was able to deliver. The resonance viewpoint was preferred over the molecular-orbital viewpoint, not because the former was theoretically more appealing, nor because it was mathematically more precise, and not even because it was empirically more satisfying. The bottom line was that resonance viewpoint was preferred because it was more congenial to the organic chemists, and because it bore a close affinity to the organic chemists' culture. Pauling became the hegemonic presence of quantum chemistry, culminating in the publication of his classic *The Nature of the Chemical Bond*. One senses that for Pauling the inability to gain the consensus of all, including Wheland, must have been hard to accept. After all, it proved that the ontological status of resonance remained an unsettled issue. The chemical community appropriated 'his' resonance theory, used it in many practical applications, accompanied the debates over its ontological underpinnings through standard textbooks, but did not necessarily subscribe to his own ontological commitments which never gathered consensual assent even among advocates of resonance theory.

Almost all of the protagonists were aware and worried about the pitfalls concerning the ontological status of the various theoretical entities. What is resonance theory about? What is the evidence in proof or disproof of the resonance theory? Is the convenience of the theory a proof or a corroboration of the theory? Is the resonance theory essentially a theory with physical meaning, or a mathematical technique or both? Has the resonance theory a basis in related sciences, such as physics? Is the resonance theory applicable in all aspects of chemical valence or is it in conflict?<sup>13</sup> Chemical developments did not become dependent on the (particular) answers given to these questions, but the community became aware that the development of quantum chemistry was not impervious to such considerations of a basically philosophical character. Nor were they indifferent to questions such as those of visualizability: what could be visualized may, perhaps, be real. Such issues were coming up again and again in review articles, popular writings, and public addresses.

Were all chemists convinced of Lewis' and Pauling's methodologies of appropriation of physical concepts, before adopting their overall approaches? Were chemists worried about the ontological status of the newly introduced entities? Were chemists sensitive and responsive to the outcome of the controversies between the protagonists regarding these issues? The answer is no: some were, but most were indifferent, independent of the legitimizing strate-

gies the protagonists' devised in order to establish their theories. But both – those who were sympathetic and those who were indifferent – were eventually passionately committed to new schemata of concepts, for the simple reason that such commitment helped them do good chemistry. We are not claiming that chemists were guided *exclusively* by the criteria Lewis and Pauling had insisted upon for the adoption of their approaches. We are, however, arguing that new methods for appropriating physical concepts, new theoretical schemata, new concepts, discussions about the ontological status of newly introduced theoretical entities, legitimizing strategies by the protagonists, effectiveness of calculational methods, *all these together and each one of them individually*, had the net effect of establishing a (new) culture for doing chemistry. And in this culture, mathematics appeared to be playing a very dominant role indeed.

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## Notes

### Abbreviations

AHQP: Archives for the History of Quantum Physics, Niels Bohr Library, American Institute of Physics.

JMP: Joseph Mayer Papers, M.I.T

PP: Ava Helen and Linus Pauling Papers, Special Collections, Oregon State University.

- <sup>1</sup> PP, Box 71, Noyes A.A. Correspondence 1921-1938, letter Pauling to Noyes, 12 July 1926, emphasis not in the original.
- <sup>2</sup> PP, Box 210, LP Calculations and Manuscripts, vol. III, 1926-1927.
- <sup>3</sup> AHQP and PP, Box 210, LP Notes and Calculations vol. III, 1926-1927, 'Work on Molecular Orbitals'.
- <sup>4</sup> AHQP, Interview with Pauling.
- <sup>5</sup> PP, Box 209, LP Notes and Calculations, vol. II 1923-1929, "1928-London's paper. General Ideas on Bonds." How Pauling came to opt for hybridization may give us an extra instance of the interaction between physical and biological modes of thought in his thought processes. See Nye 2000.

- <sup>6</sup> PP, Box 372, Chapters for Book on Quantum Mechanics of Organic Molecules, Chapter and Section Topics.
- <sup>7</sup> PP, Box 115, letter Wheland to Pauling, 20 January 1956.
- <sup>8</sup> PP, Box 115, letter Wheland to Pauling, 20 January 1956.
- <sup>9</sup> PP, Box 115, letters Pauling to Wheland, 26 January and 8 February 1956.
- <sup>10</sup> PP, Box 115, letters Pauling to Wheland, 26 January and 8 February 1956.
- <sup>11</sup> PP, Box 115, letters Pauling to Wheland, 26 January and 8 February 1956.
- <sup>12</sup> JMP, letter J. Mayer to Lewis, 29 May 1931; letter Lewis to Mayer, 4 June 1931, italics ours.
- <sup>13</sup> These were, in fact, questions prepared to be answered by the different parties in a discussion on the theory of resonance between Pauling and Soviet chemists, who had been criticizing resonance on ideological and nationalistic grounds, and in which Coulson acted as a kind of mediator of the proposed discussion suggested by The New York Chapter of the National Council of Arts, Sciences and Professions. See PP, Box 261, letter M.V. King to Pauling, 23 January 1953; letter Coulson to Pauling, 7 October 1953; letter Coulson to King, 18 January 1954; letter King to Pauling, 9 February 1954.

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