Dangerous Liaisons or Unavoidable Associations: Quantum Chemistry at the Crossroads of Chemistry, Physics and Mathematics

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Introduction

In 1967, the Swedish quantum chemist Per-Olov Löwdin (1916 -2000) in the introduction to the *International Journal of Quantum Chemistry* gave a definition of the then forty-year old discipline.[1] Written in a period in which quantum chemistry was experiencing intense growth in networking and in internationalisation and was exploring the potential of a promising instrument –the electronic digital computer– while simultaneously extending its domain to molecules of biological interest, the definition bears witness to the challenges posed at the time when contrasted with the previous state of things. It calls attention to a number of specific features of the subject-matter of quantum chemistry –the elucidation of the electronic make-up of atoms, molecules and aggregates of molecules; the interplay of theory, experiment, mathematics and computational algorithms in building the methodological apparatus of quantum chemistry; its relationship with the disciplines of mathematics, physics, and biology; and finally the assessment of the role of quantum mechanics in providing a unifying framework for the natural sciences and eventually for the life sciences.

It should be no surprise that the evolving relations of the new sub-discipline with respect to physics and mathematics caught the attention of early (and not so early) practitioners of quantum chemistry; who, implicitly or explicitly, had addressed this particular issue in scientific publications, textbooks, writings addressed to non-specialist audiences or via popular science writings. It has also caught the attention of the more historically or philosophically inclined contemporary scientists (physicists and mostly chemists) such as H. Primas, G. Woolley,

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S. Weininger, S. Shaik, W. Kutzelnigg, G. Frenking, R. Hoffman, P. Lazlo, just to name a few, who have participated or currently participate in many discussion forums, of which this conference is an example. Besides reflections offered by participants and chemical practitioners, historians and philosophers of science have contributed to the debate (in journals, journal issues, edited volumes, conferences, etc.).[2] The author's impression is that these debates have often remained trapped inside disciplinary territories, and therefore have not profited from complementary discussions on the same topics across borders.

Herein are discussed three issues which manifest the particularities of quantum chemistry, its epistemological as well as social characteristics, through the evolving articulations and rearticulations with chemistry, physics and mathematics. The first is to trace the historical evolution of quantum chemistry, by analysing those instances in its history when, to put it simply, quantum chemistry was either identifying itself primarily with mathematical physics or applied mathematics or following the semi-empirical approach so dear to chemists. The character of quantum chemistry has been formed through the gradual articulation of its relative autonomy both with respect to physics as well as with respect to mathematics. This paper attempts to argue for the historicity of this relative autonomy. The second issue is that the arguments to follow will not be solely based on what used to be called internalist considerations. Institutional parameters like the naming of chairs, university politics, networking, but also alliances quantum chemists sought to entertain with practitioners of other disciplines were quite decisive in forming the character of quantum chemistry. These two issues also bring forward an intriguing feature of the development of quantum chemistry, that is, its contingent character. It will become apparent that quantum chemistry could have developed differently, and the particular form it took has been historically conditioned. The third point to be discussed is that the gradually articulated relative autonomy of quantum chemistry, and the culture of quantum chemists which had been rather well formed by the early-1960s, was transformed dramatically with the advent of the first digital computers: the main liability of quantum chemistry, the impossibility to perform analytical calculations, was, all of a sudden, turned into an invaluable asset for the further legitimisation of electronic computers. In the early-1960s it appeared that a whole subject depended on this particular type of instrument in order to produce trustworthy results. For roughly 40 years quantum chemists had a large spectrum of methodological, philosophical, and ontological choices as well as a great flexibility in their (inter)disciplinary collaborations and alliances in order to form their idiosyncratic culture. But in a very short while electronic computers undermined the fundamental criterion with respect to which they had made their choices during this preceding phase:

though computations were still impossible to be performed analytically, they could now be made in ways all agreed to be reliable and reach a sophistication and accuracy dependent on the needs of each quantum chemist. The members of a whole scientific community who had, through an historically complicated process, achieved a consensus as to what exactly it is that they were practicing, all of a sudden, became subservient to the limitless possibilities of computations provided by digital electronic systems.

This review concentrates on the period starting with the emergence of quantum chemistry (1927) and ends in the mid-1970s, after the first decades of electronic digital computers. Here in, due to constraints of time and space, the discussions of the relationships of quantum chemistry to biology are excluded. This is a fascinating topic worthy debating especially following the extended use of electronic computers after the 1960s which enabled quantum chemistry to encompass macromolecules and molecules of biological interest.

Positioning quantum chemistry

Naming a new sub-discipline

Evidence of the difficulties encountered in positioning the new field in relation to neighbouring areas such as chemistry, physics and mathematics lies in the multiplicity of names attributed to it extending well into the period when Löwdin wrote the introductory note to the new journal. Extra evidence includes the different names assigned to chairs occupied by its practitioners, the titles of journals used as outlets for their publications, the names of congresses on the topic, and in the descriptions of courses taught on the subject.

The new field has been called mathematical chemistry,[3] subatomic theoretical chemistry,[4] quantum theory of valence,[5] molecular quantum mechanics,[6] chemical physics,[7] theoretical chemistry,[8] as well as by the now standard term, quantum chemistry. Although hard to certain, the first appearance of the designation "quantum chemistry" in the literature is probably that due to Arthur Erich Haas (1884 -1941), the Professor of Physics in the University of Vienna who in 1929 published *Die Grundlagen der Quantenchemie*,[9] a collection of four lectures delivered to the Physico-Chemical Society in Vienna. While this designation was not commonly used during the 1930s when the sub-discipline was carving out its identity vis-à-vis neighboring disciplines, it was increasingly used in textbooks written during and after the 1940s,[10] and finally ascended to a journal's title, thanks to Löwdin's creation of the *International Journal of Quantum Chemistry* in 1967.

Increasing specialisation fostered by the steady application of computer programs in solving chemical problems gave way in 1980 to the appearance of the *Journal of Computational Chemistry* and to the split of quantum chemistry into two, computational and non-computational quantum chemistry.

The uncertainty over naming the new sub-discipline, extended over a period of at least 40 years within the overall context of the impossibility of analytical computations. It faded away with the acknowledgement of its autonomous status, to give way shortly to a discussion of new avenues of specialisation opened up by the appropriation of a new tool –the computer. At the same time it forced the community to assess its impact, to choose among diverging methodological viewpoints and cover broader areas of organic, inorganic and bio-chemistry. It also acted as a bond among different groups of practitioners, at a time in which computers were few, big and expensive, so that acquiring a share of computer time became an index of survival fitness. In a quite vivid way, the multiplicity of alternative names used in the first decades, succeeded by stabilisation into "quantum chemistry", and followed by appending an adjective to the name as a mark of increasing specialisation (computational quantum chemistry, quantum biochemistry,) illustrates very forcefully the evolving identity of the new sub-discipline.

The emergence of quantum chemistry: the appropriation of physics into the chemists' culture

The traditional narrative on the history of quantum chemistry as generally offered by chemists is built around the conflict between two alternative computational methods to deal with valence problems: the Heitler-London-Slater-Pauling valence bond method (VB) and the Hund-Mulliken method of molecular orbitals (MO). Elsewhere I have proposed an alternative scheme of historical analysis centered on methodological rather than on computational criteria. Specifically, that the views of participants on theory building and the role of theory in chemistry form a set of criteria that justifies a different classification: the Heitler-London approach versus the Pauling-Mulliken approach, or to put it briefly, the "German approach" versus the "American approach".[11]

Walter Heitler (1904-1981) and Fritz London (1900-1954) accepted that the underlying laws governing the behavior of electrons were already known and, hence, to do chemistry meant simply to deal with equations which were soluble in principle even though in practice they may only produce approximate solutions. They insisted on an approach centred on the input from physics and mathematics not only in relation to the tools to be used but also as to foundational issues. Their

approach to quantum chemistry, dubbed the "German approach due" points to the existence of a group sharing the same values and including other physicists such as Friedrich Hund (1896-1997) and Erich Hückel (1896-1980), was grounded on the first principles of quantum mechanics.[12] Antagonistic to classical chemical modes of representation which relied on pictorial representations – called by Mary Jo Nye the "paper and pencil" tradition within chemistry,[13] they took seriously the inherent non-visualisability of quantum mechanics.

Linus Pauling (1901-1994) and Robert Sanderson Mulliken (1896-1986) thought differently about how the newly developed quantum mechanics could, in practice, be applied to problems of chemistry and, more specifically, to the problem of the chemical bond. By making ample use of semi-empirical methods involving a combination of quantum mechanics, empirical data and pictorial imagery, they developed their respective approaches, whose only criterion for acceptability was practical success. Most significantly, they both shared a common outlook on how to construct their theoretical schemata, on the constitutive features of their theories, on what the relation of physics to chemistry should be, and on the discourse they developed to legitimise their respective theories.

Especially until the late 1930s, there was a strong interaction between the "American" and the "British", who in the meantime had entered the field, and the "German" communities. At the same time there emerged a consonance between the "American" and the "British" approaches in the aims, tools and methods to be used by the discipline. In a sense the "pragmatic" approach of the Americans with its stress on "chemistry" and "rough semi-empirical approximations" was succeeded and complemented by the British emphasis on "mathematics". The first generation of British quantum chemists, which included J.E. Lennard Jones (1894-1954), D. Hartree (1897-1958) and C.A. Coulson (1910-1974), perceived the problems of quantum chemistry first and foremost as problems in calculation, and by devising novel calculation methods tried to bring quantum chemistry within the realm of applied mathematics.[14] Their undertaking was particularly effective if not as thrilling as that of the "Germans" or the "Americans". In this new context, demand for extra rigor was not primarily a demand for a rethinking of the conceptual framework, but rather for developing as well as legitimising mathematical techniques and methods to be used in chemical problems, and that meant they had to get involved with applied mathematics.

This impressionistic characterisation of the discipline in its early days is presented with the purpose of illustrating how much the main task of early practitioners depended on the articulation of quantum chemistry as a sub-discipline within chemistry, partially autonomous in relation to physics and mathematics, despite

being grounded on the mathematical underpinning of quantum mechanics and on the appropriation of quantum mechanical concepts. At the same time their activities carved out an identity for quantum chemistry, some of them offered explicit reflections on the relations of chemistry to physics which stemmed from their daily experience either as participants in preparing the ground for quantum chemistry to appear or as founders and early builders of the new sub-discipline. G.N. Lewis (1875-1946) and N.V. Sidgwick (1873-1952) are examples of the first group and Pauling and Mulliken of the second group.

In a paper published in the first volume of the new *Journal of Chemical Physics* (1933), Lewis opposed the analytical features of chemical theories and the convergent method of chemists to the synthetic characteristics of physical theories and the divergent method of physicists. Chemical theories were, he said, grounded on a large body of experimental material from which the chemist attempts to deduce a body of simple laws which are consistent with the known phenomena;[15] physical theories postulate laws governing the mutual behavior of particles and then attempt "to synthesise an atom or a molecule".[16]

Sidgwick, one of the most outspoken advocates of resonance theory in the U.K., gave a set of lectures on the covalent link in chemistry while visiting Cornell in the same year the *Journal of Chemical Physics* first appeared (1933).[17] The introductory lecture discussed "The relations of physics and chemistry." Reasoning along the same lines as Lewis, Sidgwick stressed that the division of scientific knowledge into different provinces was a human-made construct grounded on the acceptance of an increasing scale of complexity in the objects of study when going from mathematics to physics, chemistry and biology. An obvious consequence of increasing complexity was that "the simpler the problem you are examining the more precise is the knowledge you can acquire of it".[18] While the physicist can restrict his research to ideal systems and to tractable materials, the chemist is forced to extend his work to all pure substances. Therefore, his knowledge of their behavior is necessarily less detailed, less accurate, less deducible from first principles than that of the physicist, and to a still higher degree that of the mathematician.

Sidgwick noted that the frontiers between the various sciences were being crossed at an increasing pace. The line separating mathematics from physics was becoming blurred whilst that between physics and chemistry had vanished as a consequence of the recent development of chemistry along "molecular-mechanical" lines. He realised that "both sciences [physics and chemistry] are now examining the same problems. It is true that they use different methods, but they apply them to the same materials".[19] He was soon to participate in the popularisation of

Pauling's resonance theory, which after all fulfilled his sharp assessment – it was an embodiment of structural theory, which he elected as the paradigm of a chemical theory, in "molecular-mechanical" lines. As Pauling went further, he was to claim a reformation of the whole of chemistry from the standpoint of resonance theory. This agenda had far reaching implications in the status of chemistry within the hierarchy of the sciences. Pauling believed in the "integration" of the sciences,[20] which he deemed to be achieved through the transfer of tools and methods, the most important kind of transfer being what he called the "technique of thinking". He came to view chemistry, and specifically resonance theory, as playing a pivotal role within the physical and biological sciences, to such an extent that he regarded that chemistry now occupied the central place, formerly attributed to physics.

Mulliken did not go so far. He differentiated chemistry from physics in terms of the distinct attitudes of chemists and physicists: "Chemists love molecules, and get to know them individually (…) But what about physicists? My impression is that they are more concerned with fields of force and waves than with the individual personalities of molecules or of matter, except perhaps in the case of high-energy particles".[21] He depicted the dynamic features of the relation of chemistry to physics in terms of a wave analogy. Tidal waves inundate chemistry from time to time. Big tidal waves are relatively rare, small waves are more frequent events. Big tidal waves are composed of small waves. Mulliken identified the first big tidal wave with the emergence of physical chemistry; the next big tidal wave with chemical physics, perhaps "a modern and even more physical variety of physical chemistry".[22]

As has been shown, in the negotiations involving the status of quantum chemistry, a central place was occupied by the assessment of its relations to chemistry and physics either revealed by the actual practice of scientists or addressed explicitly in their considerations on the topic. Historians and philosophers of science have also addressed the same issue. They have repeatedly couched their discussions by referring back to Paul A.M. Dirac's 1929 statement as an illustration of the reductionist attitude of most physicists (or physically oriented scientists) involved in one way or another with the emergence of quantum chemistry. In fact, in the opening paragraph of his paper, "Quantum Mechanics of Many-Electron Systems", Dirac (1902-1984) could announce that "the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble".[23]

A large number of historically interesting questions, offering a new perspective on the topic of reductionism, can be asked in relation to Dirac's claim. How did chemists themselves, or those who worked in the field that became known as quantum chemistry, react to Dirac's claim? Did they feel threatened by physicists who felt they could do their job better than themselves? Did they feel indifferent, or did they simply not care? One way to answer these questions is to examine the research papers of chemists that specifically *cited* Dirac's 1929 paper.[24] Was Dirac's paper cited often? Why was it cited? Did chemists specifically cite Dirac's opening paragraph, or just part of it? When they referred to Dirac's claim, why did they do it? What did they consider to be its implications? How did they react to them?

Analysis based on the "Science Citation Index" data base has revealed that seldom has Dirac's paper been cited for its introductory paragraph. Furthermore, analysis showed that the very few chemists who cited Dirac's claim did not take it as a philosophical statement. On the contrary, they took it as a *historical* prediction about the future of chemistry that was, in time, proven wrong. Chemists viewed Dirac's claim as a historical statement because of his inability to predict the importance of relativistic effects and exact computations for chemistry. Historians and philosophers could also look at Dirac's claim as a *historical* rather than as a *philosophical* statement, voiced by one of the most un-philosophical of the founders of quantum mechanics, and expressing his belief that chemistry would become part of physics, and by extension that theoretical chemistry would become an even more physical form of physical chemistry. Seen from this vantage point, Dirac failed to predict that quantum mechanics soon would become a major preoccupation of chemists, and not just of physicists. He did not foresee that a new breed of chemists would appear who shared a culture very different from the reductionist culture of physicists, who embraced different methodological and ontological commitments, and who in this way would be able to attack problems of quantum chemistry successfully.

Parallel trends in disciplinary development: the uneasy relation of chemists with mathematics

Perhaps, as remarked in an earlier paper,[25] reductionism is the physicist's epistemological world-view but not the chemist's, therefore if one wants to discuss a number of questions pertaining to chemistry reductionism might be a misplaced category. Perhaps the notion of reductionism expresses a point of view dear to physicists but not to chemists. Though physicists took for granted that chemistry

would be reduced to physics, chemists did not have the luxury of waiting for the fulfillment of that vision. Reductionism may have been a research agenda, but it was one that was impossible to realise, because right from the outset, neither physicists nor chemists could deal analytically with any other molecules except for the simplest of all and even then only in grossly approximate terms.

Are there any other dimensions to reductionism, whose discussion may be considered more fruitful in addressing the same set of problems? Here it is useful to discuss the uneasy relationship of chemists to mathematics and to argue that chemists' relationship with the appropriation of mathematics into their culture was far more complex and difficult than their appropriation of physics. And though the two cannot be considered as totally independent of each other, it can be argued that chemists were more resistant to accepting the use of mathematics rather than the physical concepts, and the physical techniques.

Like any form of appropriation, opinions on the appropriation of mathematics differed among the members of the chemical community –ranging from acceptance to resistance– and can be traced back to different periods of the development of chemistry.[26] The next focus is on identifying this uneasy relationship in the emergence of quantum chemistry. While initial statements by scientists such as Pauling and van Vleck announced the rise of "mathematical chemistry" by calling attention to the potentialities associated with the mathematical apparatus attendant to the formulation of quantum mechanics,[27] in the following period, most of those who successfully managed to establish quantum chemistry as a new subdiscipline were eager to point to the subordinate role of mathematics in the sense of its computational paraphernalia. This was not just a rhetorical strategy to cater to wider audiences, but became a constitutive ingredient of quantum chemistry itself.

Pauling managed to present a coherent treatment of the chemical bond which was appealing to the chemists because of its frequent reliance on the "chemists' intuition", and the use of a lot of existing experimental data to be able to explain or predict other experimental data.[28] Though he repeatedly stressed that the understanding of the nature of the chemical bond, built on the appropriation of the quantum-mechanical concept of resonance, was possible only because of the developments due to quantum mechanics, his use of detailed mathematical formulations was reduced to a bare minimum.

In his widely-read textbook, *Valence* (1952), Coulson argued for the mathematisation of quantum chemistry at the same time he considered that quantum chemistry should be understandable by chemists with no mathematical training. The

presentation of the principles of quantum mechanics was circumscribed to two introductory chapters, and in many instances mathematical results were illustrated or complemented by the extensive use of visual representations. This was an implicit acknowledgment that visualisability, instead of elaborate mathematics, still remained one of the constitutive features of chemistry. The message was clear: quantum chemistry is not another instance in the application of quantum mechanics but a new sub-discipline of chemistry. Coulson eagerly emphasised the special role played by the alliance of experimental results and chemical intuition in the suggestion of particular mathematical developments, to such an extent that he had no qualms in asserting that "the theoretical chemist is not a mathematician, thinking mathematically, but a chemist, thinking chemically".[29] He insisted on this point time and again in meetings, lectures and review papers.

The role and importance of mathematics was to play centre stage not only in the articulation of Coulson's practice as a scientist and textbook writer but also in popular science lectures addressed to wider audiences.[30] In the Tilden Lecture delivered before the Chemical Society and in his inaugural address as Rouse Ball Professor of Applied Mathematics, both delivered around the time *Valence* came out, Coulson expressed an opinion at odds with that voiced by Dirac in 1929, and asserted that the importance of mathematics for quantum chemistry was not to be found at the computational, but rather at the conceptual level. Quantum chemistry was presented as a branch of applied mathematics, an area positioned between pure mathematics on the one hand, and experimental physics and chemistry on the other, but should never become "an appendage of experiment," just as in the same way it should never "degenerate into a bastard form of pure mathematics".[31] The true contribution of quantum mechanics to chemistry was that it showed how the concepts of the experimental chemist fitted together, how "they have all one single rationale; and how this hidden relationship to each other can be brought out".[32]

These cases have been noted not in order to make any conclusive argument about the relationship of chemists to mathematics, but rather as indicative instances of a trend among chemists which has often been bypassed in the historical and philosophical literature on quantum chemistry. As quantum chemists were assessing how physics could be appropriated into their own culture, there was a parallel and relatively independent discussion among them concerning their appropriation of mathematics. This discussion has gone unnoticed especially due to a shift of attention to the phase in which electronic digital computers were readily adopted in the hope of solving the mathematical difficulties insurmountable without them.

Different cultures within quantum chemistry: the impact of electronic digital computers

In the aftermath of WWII, in 1948, a meeting was convened in Paris to discuss the most pressing problems faced by all those interested in quantum chemical questions. Among those, that required from the community a concerted effort, were the calculation of molecular integrals involving more than two centres, their tabulation and the numerical results. Three years later, a small group of scientists gathered in Shelter Island, in 1951, to evaluate the results of the actions taken since 1948, and to outline major research strategies. Considered a "watershed", the conference aimed at obtaining formulas for the troublesome multi-central integrals which acted as "bottlenecks" to the integration of Schrödinger's equation in the *ab initio* manner. These formulae thus became available to the community of quantum chemists in standardised tables. While at first dependent on human calculations aided by desk calculators, the program soon evolved to form an efficient cooperative network that took advantage of the slowly increasing number of electronic digital computers available to the international community.[33] Their use in quantum chemistry made it possible to seriously consider the delineation of an extensive program of "completely theoretical" (*ab initio*) calculations. They turned into essential tools to calculate the time-consuming integrals of the increasingly sophisticated versions of the MO method (Pariser-Parr-Pople, Self Consistent Field, Hartree-Fock, Configuration Interaction, etc.) and in many instances replaced laboratory experiments as sources of new data, especially in the investigation of molecules otherwise inaccessible to experimentation. It was, in a way, an old dream come true. These calculations contrasted with those "semi-empirical" ones, in which the impossible analytical calculation of certain parameters was substituted by the introduction of their values as given by experimental determinations, and which had become one of the constitutive aspects of quantum chemistry since its early days.

The Conference on Molecular Quantum Mechanics held at Boulder, Colorado in June 1959, was the first major meeting of its kind since the Shelter Island Conference. It was also the first meeting where the many theoretical chemists started to realise that there were divisions separating into different groups within the community of quantum chemists. In the after-dinner speech delivered at the end of the conference, Coulson emerged as one of the more sensitive observers of this situation. For once, Coulson did not preach tolerance but advocated partisanship.[34] He announced the splitting of the community into two distinct groups – Group I included the *ab-initionists* who were interested in exact calculations in molecules including up to 20 electrons, and thus were eager to explore the poten-

tialities of electronic computers; Group II included the *a posteriorists* who remained faithful to semi-empirical methods and denied the importance of exact calculations for quantum chemistry. The split resulted from diverging views concerning the use of large-scale electronic computers.

It was however an oversimplification to reduce the difference among quantum chemists to a difference on their reliance on electronic computers. In their desire for complete accuracy, Group I appeared to be prepared to "abandon all conventional chemical concepts and simple pictorial quality in their results". Against this, the exponents of Group II argued that chemistry is still an experimental subject, whose results are built into a pattern around quite elementary concepts. Coulson did not make any effort to conceal that his sympathies lay with the latter, and re-emphasised that the role of quantum chemistry is to understand these concepts, and to show the essential features of chemical behavior. Nevertheless, he was also aware that none of these concepts could be made rigorous.

The new turn in the discipline due to the impact of computers was discussed by many others. Did Coulson's worries strike a sympathetic chord or was Coulson isolated in his assessment of the situation? It is useful to use as a probe the opinions of two quantum chemists whose research programs took advantage of the increasing relevance of computers for large molecules. One such opinion comes from the Italian Enrico Clementi (1931-), one of Mulliken's former students, working at the IBM Research Laboratory, expressed in the first volume of the *International Journal of Quantum Chemistry* (1967). Clementi was very assertive in claiming that computers could be extremely useful in the future if, and only if, one departed from the present trend in computational chemistry which pointed "toward the formation of an enormous library of wave functions with little attention to chemistry as such. This, of course, will lead to chemistry but only if we compute a very significant fraction of the possible molecules. Such a goal seems most unrealistic".[35] He reacted against the increasing "computation" of the discipline if "computation" implied its exclusion from chemical problems. Quantum chemistry without chemistry seemed to be pointless. For him, the only meaningful way to use computers was to write computer programs able to cope with realistic chemical problems such as those occurring in nature. The mathematical model behind such endeavor was, of course, quantum mechanics with as many approximations as a chemical problem could afford to sustain "before becoming an irrational "soup" of floating numbers of questionable physical meaning".[36] Then if the computer program was meant to solve a "synthetic chemistry problem", it should be able to start from the component atoms and arrive at the final molecule. If the program was written to solve a "spectroscopic problem," it should give the

basic spectroscopic constants. If the problem was a "structural problem" the computer program should give internuclear distances and electronic density mappings.

Also at the 1970 Symposium on *Aspects de la Chimie Quantique Contemporaine* held in Menton, France and organized by the C.N.R.S., Alberte Pullman (1920-), one of the founders of quantum biochemistry in France, noted that the concern for getting better and better values of parameters, integrals, or other quantities, gave the impression that for some quantum chemistry aimed solely at "the reproduction of known results by means of uncertain methods," contrary to the other sciences which aimed at "using known methods to search for unknown results".[37] She recalled Coulson's analysis at the Boulder Conference, and his views of the splitting of the community into contending parties, but did not endorse Coulson's pessimistic evaluation. She predicted that a new period in the history of quantum chemistry was just starting and that quantum chemistry's lost unity would soon be recovered. As a consequence of the development of techniques to study all valence electrons, and by extension all electrons, in molecular systems, the split between *ab-initionists* and *a-posteriorists* was to give way to the merging of both groups into one single group, which she named the *ab-initio for everybody* group. She added that she feared that "the only division that will persist between quantum chemists will be … that between wealthy and poor, those who have the means to carry sophisticated calculations and those that do not have them".[38] Above all, she hoped that the changes will "re-chemistrise" quantum chemistry.

In the interim, Coulson softened his position. He came to recognise that the divorce in the quantum chemical community which haunted him in the early days converged in time into a peaceful cohabitation of two different cultures of practitioners. Few months before his death, in the inaugural lecture as Professor of Theoretical Chemistry (1973) in the new Department of Theoretical Chemistry at the University of Oxford, Coulson recognised that the approaches of the two groups were not in mutual conflict. Both were needed, and complemented each other, so that "the particular approach which a person makes to the use of a computer almost determines his judgment on the relative merits of the two types of study".[39]

Computers enabled numerical values to be obtained as accurate as those found with the best experiments. But, still, they were just a highly refined tool, like a spectroscope or a calorimeter. Even if Coulson assessed their status as an extra instrument available to chemists, whose ready adoption impinged on experiment – chemistry's most central feature, he was sure that they were never going to replace laboratories and laboratory work. Their extensive use in quantum chem-

istry also prompted him to reassess the role of mathematics in chemistry and to go deeper in the differentiation of the inputs from physics, mathematics and computation in carving an identity for quantum chemistry. A computer gives numerical values of quantities, but cannot give explanations. To achieve an understanding of what is going on, concepts are needed, all of which lie outside the domain of strict observability, but all of which belong to the framework of chemical theory. And the ability to devise concepts of value, weaving them into the "growing pattern of chemistry," is what characterises the great chemists and distinguishes them from the "numerologists". The fun and interest of mathematics definitely did not lie in ever more sophisticated computations thanks to ever more powerful and eventually cheaper computers. In quantum mechanics as it evolved, mathematics had become central to the understanding of the chemical and physical behaviour of atoms and electrons in a way it had never been before. Previously, chemists used mathematics after a model had been devised to deal with some chemical situation, because an equation had to be solved. In these instances, to which chemists were already accustomed, mathematics was peripheral to the chemical situation, stemming as it were from the "outside". Assessing the long, and at time tortuous, way traversed in the meantime, Coulson, one of the most insightful of all quantum chemists, reiterated once again that both physics and mathematics entertained central links to chemistry, not independent from each other, but never reducible to computations, however sophisticated they might become.

Acknowledging the existence of different trends among groups of quantum chemists, at first clearly antagonistic then becoming non-conflicting or even complementary, and dependent on their opposite views on the use of computers, meant, above all, the recognition that a new culture of doing quantum chemistry was asserting itself and was carving a place in parallel with the more traditional one. That this was possible without disrupting altogether the community of quantum chemists bears witness to its maturity level and the existence of shared values which resisted confrontation with new ones. The question cannot be reduced to the realisation that computers started more or less to dictate to quantum (and theoretical) chemists the kinds of problems they would work on and the ways to deal with these problems. In the process, a new culture emerged identified by a novel style of scientific thinking, in which the increasing complexity of molecular problems was dealt with by means of mathematical modeling, that is, in which the articulation of mathematical models and their computer simulation was accompanied by graphical, numerical or analytical representations.[40]

Concluding remarks … or metaphors and their various meanings

The ability to bridge boundaries between disciplines was perhaps the most striking and permanent characteristic of those who consistently contributed to the development of quantum chemistry. Moving at ease between physics, chemistry, and mathematics, became a prerequisite to be successful in borrowing techniques, appropriating concepts, devising new calculation methods and developing legitimising strategies. With the era of computers and the development of computer science, quantum chemists were among the first scientists to explore the potentialities of the new tool, and even to collaborate in its development. In this way, they also became participants in what many dubbed as the Second Instrumental Revolution in chemistry.[41] The discussion over changing practices and their implications for the evolving identity of quantum chemistry shows how the history of quantum chemistry illustrates one of the trends which more forcefully characterises the sciences in the twentieth century – the exploration of frontiers and the crossing of disciplinary boundaries, reinforced by the mediation of many new instruments and tools.

If in the case of quantum chemistry this process was associated with its progressive de-conceptualisation while computational and graphical methods took over is a question which still needs extra research. Here in is proposed an alternative metaphor, a change from a geographical one –involving territories, boundaries and bridges– to a biological one –centered on an artificial fiber. It relates to one of the participants in the story, Coulson. To highlight "how much the validity of the scientist's account depends on the degree of interlocking between its elements", Coulson called attention, in a quite different context from that of quantum chemistry, to the fact that "the strength of an artificial fiber depends on the degree of cross-linking between the different chains of individual atoms".[42] In the same manner, one might argue that the explanatory success of quantum chemistry throughout successive developmental stages rested on the degree of interlocking among constitutive elements – chemical concepts, mathematical notions, numerical methods, pictorial representations, experimental measurements – to such an extent that it was not the relative contribution of each component that mattered, but the way in which the whole was reinforced by the *cross-linking* and *cross-fertilisation* of all elements. Furthermore its success depended not only on epistemological but also on social aspects of this *cross-fertilisation*. It involved the establishment and permanent negotiation of alliances among members of a progressively more international community of practitioners, intense networking, and adjustments and re-adjustments within the community, both at the individual,

institutional and at the educational level – in short it involved a gigantic rearrangement in the material culture of quantum chemistry.

References and Notes

[1] Per-Olov Löwdin, "Program," *International Journal of Quantum Chemistry* 1 (1967), 1-6, 1: "Quantum chemistry deals with the theory of the electronic structure of matter: atoms, molecules, and crystals. It describes this structure in terms of wave patterns, and it uses physical and chemical experience, deep-going mathematical analysis, and high-speed electronic computers to achieve its results. Quantum mechanics has rendered a new conceptual framework for physics and chemistry, and it has led to a unification of the natural sciences which was previously inconceivable; the recent development of molecular biology shows also that the life sciences are now approaching the same basis. Quantum chemistry is a young field which falls between the historically developed areas of mathematics, physics, chemistry, and biology."

[2] Journals in which debates surfaced include *Synthese*; *Hyle*; *Foundations of Chemistry; British Journal History of Science*; *Studies in the History and Philosophy of Modern Physics*; *Studies in the History and Philosophy of Science*; *Historical Studies in the Physical Sciences.*

[3] J.H. Van Vleck, "The new quantum mechanics," *Chemical Reviews* 5 (1928), 467-507; Application for the Guggenheim Fellowship, late 1925, Pauling Papers, Box 142, CIT Course Materials, Notes 1922-1930, Tau Beta Pi, CIT Transcripts, "Plans for Study".

[4] Linus Pauling, "The application of quantum mechanics to the structure of the hydrogen molecule," *Chemical Reviews*, 5 (1928), 173-213.

[5] J.H. Van Vleck and A. Sherman 1935, "Quantum Theory of Valence," *Reviews of Modern Physics*, 7 (1935), 167-227.

[6] Conference on Molecular Quantum Mechanics, University of Colorado at Boulder, June 21-27, 1959.

[7] This designation appeared for the first time with the creation of the *Journal of Chemical Physics* in 1933. Other journals used previously as outlets for papers on the new area included the *Journal of the American Chemical Society*, *Physical Review*, to be followed afterwards by journals such as *International Journal of Quantum Chemistry* or the *Journal of Computational Chemistry*.

[8] J.E. Lennard-Jones occupied the first chair of Theoretical Chemistry in the world in 1932, but C.A. Coulson was just offered an equivalent chair in Oxford in 1973.

[9] A.E. Haas, *Die Grundlagen der Quantenchemie* (Leipzig: Akade. Verl., 1929), English translation *Quantum Chemistry. A short introduction in four non-mathematical lectures* (London: Constable & Company, 1930), translated by L.W. Codd.

[10] Examples are Henry Eyring, John Walter, George Kimball, *Quantum Chemistry* (Wiley Publishers, 1944); Kenneth Pitzer, *Quantum Chemistry* (New York, Prentice-Hall, 1953); Walter Kauzmann, *Quantum Chemistry, an Introduction* (New York: Academic Press, 1957).

[11] Kostas Gavroglu and Ana Simões, "The Americans, the Germans and the Beginnings of Quantum Chemistry: The Confluence of Diverging Traditions," *Historical Studies in the Physical Sciences,* 25 (1994), 47-110.

[12] A. Karachalios, "On the making of Quantum Chemistry in Germany," *Studies in the History and Philosophy of Modern Physics*, 31B (2000), 493-510.

[13] Mary Jo Nye, "Paper Tools and Molecular Architecture in the Chemistry of Linus Pauling," in U. Klein, ed., *Tools and Modes of Representation in the Laboratory Sciences* (Dordrecht: Kluwer Academic Publishers, 2001), pp.117-132.

[14] Ana Simões and Kostas Gavroglu, "Quantum Chemistry *qua* Applied Mathematics. The contributions of Charles Alfred Coulson (1910-1974)," *Historical Studies in the Physical Sciences*, 29 (1999), 363-406; Ana Simões and Kostas Gavroglu, "Quantum Chemistry in Great Britain: Developing a Mathematical Framework for Quantum Chemistry," *Studies in the History and Philosophy of Modern Physics*, 31 (2000), 511-548; Kostas Gavroglu and Ana Simões, "Preparing the ground for quantum chemistry to appear in Great Britain: the contributions of the physicist R.H. Fowler and the chemist N.V. Sidgwick," *British Journal for the History of Science*, 35 (2002), 187-212.

[15] G.N. Lewis, *Anatomy of Science* (New Haven: Yale University Press, 1926), 172-174; G.N. Lewis, "The Chemical Bond," *Journal of Chemical Physics*, 1933, 1, 17-28; G. N. Lewis, *Valence and the Structure of Atoms and Molecules* (New York: The Chemical Catalog Company, 1923, reprinted by Dover Publications, 1966), pp. 20-21.

[16] Lewis, "Chemical Bond," op.cit. (15), 17.

[17] Gavroglu and Simões, "Preparing the ground", op.cit. (14).

[18] N.V. Sidgwick, *Some Physical Properties of the Covalent Link in Chemistry* (New York: Cornell University Press, 1933), 3, 4.

[19] *Ibid*., 3.

[20] Linus Pauling, "The place of chemistry in the integration of the sciences," *Main Currents in Modern Thought*, 7 (1950), 108-111 in Barbara Marinacci, ed., *Linus Pauling in his Own Words* (New York: Simon & Schuster, 1995), pp. 107-111.

[21] R.S. Mulliken, "Spectroscopy, Quantum Chemistry and Molecular Physics," *Physics Today*, 21 (1968), 52-57, on 54.

[22] Ibid, 56.

[23] P.A. M. Dirac, "Quantum Mechanics of Many-Electron Systems," *Proceedings of the Royal Society of London A 123* (1929), 714-733, on 714.

[24] Ana Simões, "Dirac's claim and the chemists," *Physics in Perspective*, 4 (2002), 253-266. I used the Science Citation Index (1945-1979) to identify all papers citing Dirac's paper. For the period (1929-1945) which is not covered by SCI I only carried a non-systematic search of journals that include papers on quantum chemistry. I just covered a 50-year period assuming that in this period Dirac's paper became "common property" so that citations diminished accordingly to become almost non-existent afterwards.

[25] Ana Simões and Kostas Gavroglu, "Issues in the History of Theoretical and Quantum Chemistry 1927-1960," in C. Reinhardt, ed., *Chemical Sciences in the Twentieth Century: Bridging Boundaries* (Weinheim: Wiley-VCH, 2001), 51-74.

[26] Some, like Frankland, van't Hoff, W. Ostwald, G.N. Lewis, pushed quite strongly for introducing mathematics into chemistry. Even J. Larmor and J.J.Thomson before him tried to propose a mathematical framework for dealing with chemical problems. But resistance to such programs came from different quarters.

[27] Pauling Papers, Box 142, CIT Course Materials, Notes 1922-1930, Tau Beta Pi, CIT Transcripts, "Plans for Study"; J.H. van Vleck, "The new quantum mechanics," *Chemical Reviews* 5 (1928), 467-507, on 500, emphasis in original.

[28] Linus Pauling, *The Nature of the Chemical Bond and the Structure of Atoms and Molecules. An Introduction to Modern Structural Chemistry* (New York: Cornell University Press, 1939)

[29] C.A. Coulson, *Valence* (Oxford: Oxford University Press, 1952), preface, on p. v.
[30] Ana Simões, "Textbooks, popular lectures and sermons: the quantum chemist Charles Alfred Coulson and the crafting of science," *British Journal for the History of Science*, 37(3) (2004), 299-342.
[31] C.A. Coulson, *The Spirit of Applied Mathematics* (Oxford, 1953), 11.
[32] C.A. Coulson, "The Contributions of Wave Mechanics to Chemistry," *Journal of the Chemical Society* (1955), 2069-2084, 2069-2070. Coulson repeated and rephrased many of the arguments voiced in his inaugural lecture as Professor of Theoretical Physics at King's College, London, published as C.A. Coulson, "Wave Mechanics in Physics, Chemistry and Biology," *Science Progress* (1948), *36*, 436-449.
[33] W. Aspray, "Computer science and the computer revolution," in Mary Jo Nye, ed., *The Cambridge History of Science*, *vol.5. The Modern Physical and Mathematical Sciences* (Cambridge: Cambridge University Press, 2003) pp.598-614.
[34] C.A. Coulson, "Present State of Molecular Structure Calculations," Conference on Molecular Quantum Mechanics, University of Colorado at Boulder, June 21-27, 1959, *Reviews of Modern Physics, 32* (1960), 170-177.
[35] Enrico Clementi, "Chemistry and Computers," *International Journal of Quantum Chemistry*, 1S (1967), 307-312, p. 308.
[36] Ibid.
[37] Alberte Pullman, "Propos d'Introduction. 1970: Bilan et Perspectives," *Colloque International sur les Aspects de la Chimie Quantique Contemporaine*, 8-13 July 1970, Menton, France, organized by R. Daudel et Alberte Pullman (Paris: Editions du CNRS, 1971), 9-16, on 13.
[38] Ibid., on 14.
[39] C.A. Coulson, *Theoretical Chemistry Past and Future* (ed. S.L. Altmann), Oxford, 1974, 20; CP, Ms. Coulson 36, B.16.4, 9.
[40] S. Schweber, M. Wächter, "Complex systems, modelling and simulation", *Studies in the History and Philosophy of Modern Physics,* 31 (2000), pp.583-609. For them, computers are central components of a Hacking-type revolution – the "complex systems computer modeling and simulation" revolution. Computers generated sweeping transformations of the social, material, economic and cultural contexts, besides introducing a new style of scientific thinking.
[41] Carsten Reinhardt, *Shifting and Rearranging: Physical Methods and the Transformation of Modern Chemistry* (Sagamore Beach, Mass.: Science History Publications, 2006). In a way this book belongs to a recent trend, to which have contributed authors such as Davis Baird, Christoph Meinel, Peter Morris, and Tony Travis, which pays particular attention to the role of instrumentation and the impact of the so-called Second Instrumental Revolution in chemistry.