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"Escaping from the thought forms of the physicists": various issues in the writing of the history of quantum chemistry

Summary – This paper deals with a number of the historiographical issues in the development of quantum chemistry. The problem of reduction of chemistry to physics appears to have been a problem that worried chemists from after the advent of quantum mechanics. The impossibility to provide analytical solutions, forced many of those who used quantum mechanics for chemical problems to devise a number of novel notions and semi-empirical methods in order to provide the theoretical framework akin to quantum chemistry. After the Second World War developments in electronic computers brought about dramatic changes in the culture and practices of quantum chemists, making the prospect of ab initio calculations a realistic prospect.

Key words: quantum chemistry, ab initio, semi empirical, computers.

In 1969 in a symposium on the *Fifty Years of Valence* Charles Alfred Coulson, the writer of the well known book titled *Valence* and Professor of Theoretical Chemistry at King's College London, was emphatically declaring that one of the primary tasks of the chemists during the initial stage in the development of quantum chemistry was to *escape from the thought forms of the physicists*[1]. Indeed. Among the many and, at times, insurmountable barriers during the becoming of quantum chemistry, perhaps the one hurdle that was the most incapacitating was the danger to develop a subdiscipline in chemistry that would be indistinguishable from a sub-

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[1] C.A. Coulson, "Recent Developments in Valence Theory: Symposium Fifty Years of Valence", *Pure and Applied Chemistry*, 24 (1970), 257-287, on 259 and 287. Emphasis not in original.

discipline in physics[2]. Hence, escaping the thought forms of the physicists was a strategic choice – not by all the protagonists, nor, even consciously pursued, but, surely, in the minds of those whose work eventually established quantum chemistry.

The bare elements of the history of quantum chemistry are well known. In 1927 Walter Heitler and Fritz London calculated by using the Schrodinger equation the strength of the homopolar bond of the Hydrogen molecule. They were able to show in no uncertain terms that the homopolar bond – a kind of mystery within the classical framework – could be mathematically tackled and physically understood by using the recently formulated quantum mechanics, and, in fact, by using the even more mysterious exclusion principle. It came to be realised that everything depended on spin this purely quantum mechanical notion. In a short while, Friedrich Hund in Germany and Robert Mulliken in the US tried to develop a different framework. They wanted to develop the Aufbau principle that Bohr had proposed for the atom, for molecules. The molecular orbital approach became an amazingly successful schema, had its basis in the understanding of band spectra and it did not involve the use of heavy mathematics. It was Linus Pauling in the early 1930s who used quantum mechanics in his own peculiar way, developed the notion of resonance and with a forceful propaganda became the dominant figure of quantum chemistry, until more sophisticated mathematical methods started developing after the second world war. It was the electronic computer which, especially after the late 1950s, brought about the deep changes in the practice of quantum chemistry.

And it was the electronic computer which in the minds of the chemists revived a nightmare first expressed by Paul Dirac.

> The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. *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.* It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation[3].

Dirac's pronouncement was an unfortunate curse upon the heads of the chemists. But fortunately, the chemists chose to ignore it and for more than a gen-

[2] For more details see Kostas Gavroglu, Ana Simões, *Neither Physics nor Chemistry. A History of Quantum Chemistry* (Cambridge: MIT Press, forthcoming 2010).

[3] P.A.M. Dirac, "Quantum mechanics of many electrons", *Proceedings of the Royal Society* A 123 (1929), 714-33, on 714, emphasis mine.

eration they devised theoretical schemata and approximation methods trying to overcome it. What Dirac says is clear: after the advent of quantum mechanics, everything can be explained in terms of physics. No point in defending the autonomy of chemistry, no point in trying to devise new theories. Everything is a matter of calculations, it may be a pity that the equations are complicated, but if in due time new methods are devised, then all of chemistry can be eaten with a spoon. What a tragic state of affairs for the chemists it must have been. Dirac expressed what was a nightmarish outlook for chemists: that chemistry was physics, and that it was only a matter of technical difficulties – that is, of the complication of the equations – that chemistry had not witnessed its death.

History, however, has a way of falsifying such pronouncements. Starting with the paper of Heitler and London, and continuing through the resonance theory of Linus Pauling and the molecular orbitals of Friedrich Hund and Robert Mulliken, the history of quantum chemistry has been a history of a subdiscipline whose protagonists were trying to circumvent Dirac's pronouncements. What appeared as a liability for all those who wanted to apply quantum mechanics to chemical problems, became an asset, since the impossibility to provide an analytical solutions forced them to devise new concepts, to formulate new theoretical schemata and to develop a new approximation methods. They did great and the wealth of conceptual contributions, new theoretical insights into the behaviour of molecules and technical mathematical developments in methods of numerical solutions, gave rise to a new subdiscipline that some called theoretical chemistry and others quantum chemistry.

But the difficulties involved in the solution of the equations were immense, almost insurmountable. These difficulties were expressed in a dramatic manner by Hartree in a report for the Physical Society published in 1948. He underlined the significance of the newly developing calculating machines by writing[4]

> It has been said that the tabulation of a function of one variable requires a page, of two variables a volume, and of three variables a library; but the full specification of a single wave function of neutral *Fe* (the common iron) is a function of seventy-eight variables. It would be rather crude to restrict to ten the number of values of each variable at which to tabulate this function, but even so, full tabulation of it would require entries, and even if this number could be reduced somewhat from considerations of symmetry, there would still not be enough atoms in the whole solar system to provide the material for printing such a table.

The development of an "in-between" discipline such as quantum chemistry can be narrated through four interrelated clusters of issues which manifest the particularities of quantum chemistry through the evolving (re)articulations of quantum chemistry with chemistry, physics, mathematics and biology, and its institutional positioning.

The first cluster involves issues related to the historical becoming of the epistemic aspects of quantum chemistry: that is, the multiple contexts which prepared

[4] Hartree (1948a), on 113.

the ground for its appearance, the ever present dilemmas of the initial practitioners as to the "most" appropriate course to choose between the rigorous mathematical treatment, its dead ends, and the semi-empirical approaches with their many promises, the novel concepts introduced and the intricate processes of their legitimization. Quantum chemistry appears to have been formed through the confluence of a number of distinct trends, with each one of them claiming to have been the decisive factor in the formation of this discipline: neither the relatively straightforward quantum mechanical calculations of London and Heitler in 1927, nor the rules proposed by Mulliken to set an *Aufbau* principle for molecules, nor Pauling's reappropriation of structural chemistry within a quantum mechanical context, nor Coulson's and Hartree's systematic but at times cumbersome numerical approximations, could be said to have given quantum chemistry its epistemic content and institutional framework. The becoming of quantum chemistry has been the result of an attitude by many physicists, chemists, mathematicians, biologists and computer experts who did not feel constrained by any of these approaches so that to be discouraged from investigating the multitude of possibilities provided by the many alternatives. Though it may appear that there is a consensus that quantum chemistry had always been a "branch" of chemistry, this was not so during its history, and different scientific communities such as physicists and applied mathematicians attempted to appropriate it.

The second cluster of issues are those related to disciplinary emergence: the naming of chairs, university politics, textbooks, meetings, networking, as well as the alliances quantum chemists sought to have with practitioners of other disciplines, became quite decisive in the formation of the character of quantum chemistry. The emergence of quantum chemistry in the institutional settings of Germany, the USA and Britain, and later on in France and Sweden, and a number of conferences and meetings of a programmatic character, helped to mould its character: a marginal activity at the beginning, it had the good luck to have gifted propagandists and able negotiators among its practitioners. Heitler's, London's and Hund's rather ascetic yet strong pleas for that chemical problems should be subjected to the rigors of first principles of quantum mechanics, Mulliken's tirelessness in familiarizing physicists and chemists with the attractiveness of the molecular orbital approach, Pauling's aggressiveness to push resonance theory as the only way to do quantum chemistry, Coulson's incessant attempts to popularise his views in order to explain the character of valence, Daudel's and Pullmans' researches into molecules with biological interest, and Per Olov Löwdin's founding of a new journal, all these, contributed towards the gradual formation of the characteristics of the emerging subdiscipline.

The third cluster of issues is related with a rather unique development in the history of this subdiscipline: the re-articulation of the practices of the community after the early 1960s which was brought about by a single instrument – the electronic computer. The fundamental disadvantage of quantum chemistry, that is, the impossibility to perform analytical calculations, was, all of a sudden, turned into an

invaluable advantage for the further legitimization of electronic computers. In the early-1960s it appeared that a whole subject depended on this particular instrument in order to produce trustworthy results. All of a sudden, ever more scientists started to realise that "quantum chemistry is no longer simply a curiosity but is contributing to the mainstream of chemistry"[5]. The prospect of *ab initio* calculations, which did not use experimental data built in the equations in any way, seemed to offer the promise of new and reliable results, and soon reached a sophistication and accuracy to serve the needs of each quantum chemist. The members of a whole disciplinary community, through a historically complicated process had attained a consensus about the coexistence of the two approaches that of valence bond and that of molecular orbitals. In a few years they became subservient to the limitless possibilities of computations provided by a particular instrument. Most of the leaders of the different traditions were nearing the end of their careers, since they had all gotten into quantum chemistry when they were very young. Fostered by the use of computers, applied to ab initio but also to semi-empirical calculations, members of the quantum chemical community recognized that a new culture of doing quantum chemistry was asserting itself and was carving a dominant place among the more traditional ones. It was identified by a novel style of scientific thinking, in which the increasing complexity of molecular problems was dealt with by means of mathematical modelling, and a burst of activities in relation to the writing and dissemination of computer programs. Eventually, it, even, became unnecessary to perform expensive experiments, since calculations would provide the required data!

The fourth cluster of issues is related to philosophy of science. It is undoubtedly the case that in recent years there has been an upsurge of scholarship in the philosophy of chemistry, and understandably quantum chemistry has played a prominent role in such a new situation. It is, also the case, that a number of papers and discussions have had as their starting point issues that have been all too common in the history of quantum chemistry. I have in mind issues such as reductionism, scientific realism, the role of theory, including its descriptive or predictive character, the role of pictorial representations and mathematics, the role of semi-empirical versus *ab initio* approaches, the status of theoretical entities and of empirical observations.

The successes of quantum mechanics in chemistry induced many to bring to the fore a number of philosophical issues about chemistry, or to discuss problems other philosophers of science had been discussing, but, now, within the context of chemistry. Reductionism turned out to be one of the pivotal issues.

These four axes – the epistemic content of quantum chemistry, the social issues involved in disciplinary emergence, the dramatic changes brought about by

[5] "Computational Support for Theoretical Chemistry", National Academy of Sciences, National Research Council, 1971, p. 1

the digital computers and the philosophical issues related to the work of almost all the protagonists—form the narrative strands of our history. Perhaps, it may be a useful way to deal with the becoming of in-between subdisciplines. It is, however, certainly the case that they appear to be indispensable for understanding how quantum chemistry developed during its first 50 years.

After the Second World War, quantum chemistry had already acquired all the characteristics of an autonomous subdiscipline. Its conceptual framework, its theoretical schemata, its textbooks, the University Chairs, the journals, the conferences had all been expressions that of a thriving community which had come to terms with the incapacitating prospect of the subdiscipline: that it is impossible to have analytical solutions to the equations.

But the 1950s saw developments that would change the everyday practices of the quantum chemists in a dramatic manner. And that was the development of the electronic computer.

Two conferences capture in a most interesting way the changes that computers would bring about: the Boulder Conference of 1959 and the Conference at Maryland in 1970. The former dealt with molecular quantum mechanics, and speakers talked about their subject within a totally new rationale when one compares it with that of other earlier conferences. It was the framework formed by the realization that powerful computing machines were making their presence felt in no uncertain terms, and that they were becoming an indispensable aspect of the future of quantum chemistry. If the Conference of 1959 was heralding a new period of quantum chemistry, the Conference held in Maryland in 1970 on Computational Support for Theoretical Chemistry mapped the future of quantum chemistry in terms of the possibilities provided by computers, not simply as machines which would facilitate the calculational work of chemists, but as instruments which would act as probes of an amazing exactness, often substituting the need for experiments. If in the deliberations of the Conference of 1959 what was reflected was that computers were to become an indispensable tool for quantum chemists, the discussions of the 1970 Conference reflected a totally new social vista: the amazing development of hardware and software, and the pivotal role of quantum chemistry in the development of computer technology as well as its mounting importance within chemistry.

Let me concentrate in the 1959 Boulder Conference. Organized by the National Science Foundation, its steering committee included Mulliken and Slater as representatives of the first generation of quantum chemists and strong believers in the promises of heavy computations. It also included some already well-known names of the younger generation such as Robert Parr, and Rudolph Pariser, both of whom worked out the approximation which bore their names. The topics to be discussed in the various sessions covered old and new themes, illustrating the incursions of the field into big molecules, the test of new calculational methods and computer programs, at the same time it highlighted the move from structure to

molecular dynamics and the consideration of forces other than the chemical bond in playing a role in quantum chemistry[6].

What makes the Boulder Conference an event with a particular interest for historians of science, was that it marked, in no uncertain terms, the transition from the founding generation of quantum chemists to a generation whose success would be dependent on the way they would make use of the electronic computers. During the Conference the promising prospects of the electronic computers was discussed together with the dangers that these prospects had for the change of the character of quantum chemistry as it had been articulated since the Heitler-London paper of 1927. Everyone was convinced that improving the calculational techniques and electronic hardware will bring forth many and new results. Not everyone agreed on the extent to which the new practices would distort accepted norms, thus reconfiguring quantum chemistry (almost) beyond recognition.

Perhaps one of Mulliken's close young collaborators at his Laboratory of Molecular Structure and Spectra at Chicago, Bernard Ransil was the person who captured best the "climate" of the meeting. His introductory paragraph is quite illuminating.

> The coming of age of the digital computer and its impact on the field of molecular structure has recently been variously characterized as "disastrous to theoretical chemistry" and as "the means which will enable modern structural chemistry to become less of an art and more of a science". Insofar as the digital computer provides the means for critical calculations upon which theoretical concepts may be justified, tested, or based, the author is inclined toward the latter point of view; insofar as the use of a digital computer might blunt one's critical faculties and stunt the free play of his scientific imagination, reducing his research to little more than calculations for the sake of calculations, he agrees with the former estimate. Obviously a wide middle ground exists where the digital computer, intelligently used as a research instrument, can quickly provide the theoretical chemists with accurate results to an illuminating but complex critical calculation. Properly used, the numerical experiment can be as much of an aid and stimulus to the theoretical chemist as a well thought out and executed physical experiment[7].

As it is clear from this initial statement, Ransil quotes views without acknowledging the sources, so that we can surmise that these views were widely circulating and were, in fact, characteristic of the shop talk of the community. These views expressed the core of a wide spectrum of opinions, which were no doubt expressed in the soul searching discussions during the conference. Interestingly, he did not uncritically embrace all promises of a golden future. But he emphasized that a

[6] R.G. Parr, "Introductory Note", Conference on Molecular Quantum Mechanics, University of Colorado at Boulder, June 21-27, 1960, *Reviews of Modern Physics*, 32 (1960), 169. Sessions dealt with atoms and small molecules, the many-body problem, density matrices, methods to deal with atoms in molecules, complex molecules, nature of the chemical bond, problems in structure and spectra, spectroscopy methods, reaction rates, and intermolecular forces.

[7] Bernard J. Ransil, "Studies in molecular structure. I. Scope and summary of the Diatomic Molecule Program", *Reviews of Modern Physics*, 32 (1960), 239-244, on 239.

number of household words for the quantum chemist such as bond order, bond length, charge density, conjugation, hyperconjugation, and resonance would "benefit from a reevaluation based upon accurate *a priori* quantum mechanical calculations"[8].

Coulson was, I think, the protagonist of the Conference, trying to express the worries of a generation that had established quantum chemistry and the aspirations of the younger practiotioners. Despite his own contributions and those of his research associates to the calculation of molecular integrals using ever more elaborate computer programs, Coulson was never oblivious of the major shortcomings of their indiscriminate use and abuse. At the end of the 1950s he started realising that deep changes had occurred within the community of quantum chemists.

Coulson gave the after-dinner speech, summing the main trends of the meeting and listing the problems he felt were to occupy the chemists in the years to come[9]. But in this speech, one senses a very worried Coulson, a Coulson who realized that there are now deep and perhaps irreconcilable divisions in the community of quantum chemists. These are divisions that he felt are absolutely detrimental to the discipline.

In discussing the major conclusions from the Conference he noted:

> There is one of these [conclusions] about which I feel very strongly, and because it is of such great importance for any future conferences on molecular structure, I make no apology for coming straight to it. It seems to me that the whole group of theoretical chemists is on the point of splitting into parts…almost alien to each other....The situation is indeed serious. For my own part, I am very far from laughing at it, and I want us to look at as openly and as dispassionately as possible. The questions that we are really asking concern the very nature of quantum chemistry, what relation it has to experiment, what function we expect it to fulfill, what kind of questions we would like it to answer. I believe we are divided in our own answers to these questions[10].

The splitting, he thought, in the community resulted from the antagonism of two extreme groups. The first group possessed great computational skills and advocated that there are a number of problems that a dispute can only settle by computation since experiments are too difficult. Examples of this were the absorption of H as a function of wavelength (very important for the astrophysical study of solar radiation) and the shape of the ground state of the methylene radical. This kind of work must have great accuracy and involved much use of electronic computers. To many people this group of chemists appeared to be moving away from the conventional concepts of chemistry, such as bonds, orbitals and overlapping hybrids "as to carry

[8] Ibid.

[9] C.A. Coulson, "Present State of Molecular Structure Calculations", Conference on Molecular Quantum Mechanics, University of Colorado at Boulder, June 21-27, 1960, *Reviews of Modern Physics*, 32 (1960), 170-177.

[10] Ibid., on 172.

the work itself out of the sphere of real quantum chemistry"[11]. On the other extreme were calculations with very rough approximations for biological molecules. These calculations give quite interesting results but the approximations put forward would be greatly upsetting to the people who used extensively computers.

"Where, in all this, does 'real' quantum chemistry lie?" Coulson wondered. The possibilities offered by the electronic computers enabled one to distinguish two levels of activity a distinction with which most of the exponents of computing at the Conference agreed. It appeared that 20 electrons may be a criterion for the upper limit to the size of a molecule for which accurate calculations are expected to become practicable. Coulson thought that there was a deep distinction between those chemists whose main interest laid in the 1-20 range, and consequently thought in terms of full electronic computation, and those who did not think in these terms. The two groups deserved distinct names Group I (the electronic computors or ab initio-ists as some would call them) and Group II (the non-electronic computors or *a posterior-ists*).

> I cannot help thinking that the gap between the two groups is so large that there is now little point in bringing them together. This is probably the last conference of the old kind. In future we should either have two distinct conferences or be prepared to plan parallel sessions for group I and II enthusiasts[12].

But he thought that it would be an oversimplification to think that the difference is only a difference having to do with the use of 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 an experimental subject, whose results are built into a pattern around quite elementary concepts. He did not make any effort to conceal that his sympathies lay with the latter and re-emphasized that the role of quantum chemistry is to understand these concepts and show what are the essential features in chemical behaviour. Nevertheless, he was also aware that none of these concepts could be made rigorous.

Coulson felt that it would be a serious loss if members of Group I did not maintain a close link with experiment and with conventional thought forms of chemistry. He felt strongly that there was a danger that Group I people will forget that chemistry is associated with the real world. He ended in a pessimistic mood.

> It is not surprising that the orientations of these two groups of quantum chemists are so different that cross fertilization has now become much less frequent than in earlier days….Many members of Group I do not realize what is happening to them; and members of both groups display an undesirable lack of sympathy for each other's work[13].

[11] Ibid.
[12] Ibid., on 173.
[13] Ibid., on 174.

A few years later, in a meeting in Paris, Alberte Pullman exhorted quantum chemists to reintroduce chemistry into their calculations and denounced the tendency on the part of many theoretical chemists to forget that quantum chemistry remained nonetheless *chemistry*, despite the possibility of increased accuracy in calculational standards due to the use of computers. The obsession 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" [14].

Whether chemistry had been forgotten in the euphoria of the age of the computer is a debatable issue. What, however, is not debatable is that from the very beginning of the period when chemical problems were examined quantum mechanically, everyone involved in the subsequent developments tried to understand the character of what was resulted from the encounter(s) of chemistry with quantum mechanics. Was quantum chemistry an application to or use of quantum mechanics in chemical problems? Was quantum chemistry the totality of chemical problems formulated in the language of physics and which could be dealt by a straightforward application of quantum mechanics with, of course, the ensuing conceptual readjustments? Or was it the case that chemical problems could be dealt with only through an intricate process of appropriation of quantum mechanics by the chemists' culture? Research papers, university lectures, textbooks, meetings, conferences, presidential addresses, inaugural lectures, even correspondence among chemists and physicists became the fora for the discussion of these questions. By attempting to provide answers to these seemingly pedantic, and often implicitly posed, questions, various individuals or groups of individuals attempted to legitimize outlooks and define the status of quantum chemistry. They attempted, that is, to achieve an agreement about the degree of relative autonomy of quantum chemistry with respect to both physics and chemistry and, hence, about the extent of its non-reducibility to physics.

Perhaps it may be argued that the involvement of almost all those who did pioneering work in quantum chemistry in the various discussions and disputes – either in their published papers or in their correspondence or in their public lectures – had to do with *legitimizing the epistemological status of various concepts in order to be able to articulate the characteristic discourse of quantum chemistry*. Legitimizing a discipline, however, is not only related to the clarification of the content of the proposed concepts and the correctness of certain approaches. The process itself is a rigorously "social" process, involving rhetorical strategies, professional alliances, institutional affirmations, presence in key journals and conferences etc.[15].

[14] Ibid, p. 13.

[15] This is very clear, for instance, when one contrasts the impact of both Hückel and Hellmann in popularizing their ideas among chemists vis-à-vis the efforts by, let us say, Pauling.

Well into the 1970s, the period, that is, when it became clear that computers will bring dramatic changes to quantum chemistry, Robert Wilson, the co-author of *Introduction to Quantum Mechanics with Applications to Chemistry* with Pauling wrote a paper examining the impact of quantum mechanics on chemistry. He posed the following questions: Is quantum mechanics correct? Is ordinary quantum mechanics good enough for chemistry? Why should we believe that quantum mechanics is in principle accurate, even for the lighter atoms? Can quantum-mechanical calculations replace experiments? Has quantum mechanics been important for chemistry? Can many-particle wave-functions be replaced by simpler quantities? Based on the ways in which computers were being used in quantum chemistry, and worried about the lack of new ideas during the last twenty years, Wilson speculated on the possibility that the "computer age will lead to the partial substitution of computing for thinking". But he hoped for "new and better schemes", and he still believed that qualitative considerations would continue to dominate the applications of quantum chemistry. This was, after all, because of the special methodology of chemistry:

> Chemistry has a method of making progress which is uniquely its own and which is not understood or appreciated by non-chemists. Our concepts are often ill-defined, our rules and principles full of exceptions, and our reasoning frequently perilously near being circular. Nevertheless, combining every theoretical argument available, however shaky, with experiments of many kinds, chemists have built up one of the great intellectual domains of mankind and have acquired great power over nature, for good or ill[16].

Wilson was encapsulating the development of quantum chemistry in an amazingly succinct, yet shocking, way. Here, there is no attempt to polish the narrative nor to turn the protagonists into heroes. Nor is there any attempt to be humble. And the message was clear: the history was messy, the result unique. From the very beginning, among the chemists, there was an ambivalent attitude towards any new proposal of "*how* to do quantum chemistry" or, rather, "*what* to do with quantum mechanics when doing quantum chemistry".

By 1970, members of the first generation of quantum chemists were in their sixties and seventies. Some had already passed away: Hellman was executed in 1938, London and Lennard-Jones both died in 1954, and Hartree died four years later, in 1958. Heitler, Hückel, Hund, and Van Vleck were not any more contributors to the discipline. Pauling had been estranged from the discipline he founded and planned to dominate. Already by wartime his attention was drifting away to problems which shaped molecular biology. In fact, still active were just Mulliken, who was awarded the Nobel Prize in 1966, Slater and Coulson. Their groups nurtured many of the members of the new generation of quantum chemists.

[16] E.B. Wilson, "Fifty Years of Quantum Chemistry", *Pure and Applied Chemistry* 47 (1976), 41-47, on 47.

Circulation, networking, exchange programs, textbooks, international meetings and summer schools were constitutive elements of the training of this whole new generation of practitioners. And they started defining the agenda of the discipline: Raymond Daudel, Bernard and Albert Pullman, Kotani and Löwdin, Parr, Pariser and Pople, Crawford, Shull, Platt, Roothaan, Scherr, Ransil, Barnett, Boys, Clementi, McWeeney, Hall, Appel, Calais, Lindenberg, Fröman, and many more. The concern for bigger molecules extended the field of application of quantum chemistry to inorganic chemistry and solid-state physics, as well as to biology, medicine and pharmacology. The change of scale, from very small molecules to big molecules and macromolecules introduced new constraints into the discussion such as the role of the environment in inducing properties in molecules. And this trend helped the emergence of Quantum Biochemistry, Quantum Biology (and to a lesser extent to Quantum Pharmacology) as well as to Computational Chemistry, Molecular Engineering and Materials Science and Engineering. In a sense, with quantum chemistry's forays in biology, medicine and pharmacy, the centuries' old relations of the discipline with the precursors to these specialties resurfaced again, in the context of a sustained relation with physics and mathematics. Even the emergence of Philosophy of Chemistry has been closely associated with Quantum Chemistry[17].

[17] David Baird, E.R. Scerri and L.C. McIntyre, eds., *Philosophy of Chemistry. Synthesis of a new discipline* (Dordrecht: Kluwer Academic Publishers, 2006); J. van Brakel, *Philosophy of Chemistry. Between the manifest and the scientific image* (Leuven: Leuven University Press, 2000); J.E. Early, ed., *Chemical Explanation: characteristics, development, autonomy, Annals of the New York Academy of Sciences*, 988 (2003); Kostas Gavroglu, "Philosophical issues in the history of chemistry", *Synthese*, 111 (1997), 283-304; *Special Issue* "*Theoretical Chemistry in the making: appropriating concepts and legitimizing techniques*", *Studies in the History and Philosophy of Science*, 31 B(4) (2000); Robin Findlay Hendry, "Mathematics, representation and molecular structure", in Ursula Klein, eds., *Tools and Modes of Representation in the Laboratory Sciences* (Dordrecht: Kluwer Academic Publishers, 2001), pp. 221-236; "Autonomy, explanation, and Theoretical Values. Physicists and chemists on molecular quantum mechanics", *Annals of the New York Academy of Sciences* 988 (2003), 44-58; "The physicists, the chemists and the pragmatics of explanation", *Philosophy of Science*, 71 (2004), 1048-1059; *The Metaphysics of Chemistry*, n/d, http://www.dur.ac.uk/r.f.hendry/; P. Janich, and N. Psarros, eds., *The autonomy of chemistry* (Würzburg: Königshausen & Neumann, 1988); Hans Primas *Chemistry, quantum mechanics and reduction* (Berlin: Springer, 1983); "Can we reduce chemistry to physics?", in G. Radnisky, ed., *Centripetal Forces in the Sciences* (NY: Pergamon Press, vol. 2, 1988), pp. 119-133; J.L. Ramsey, "Molecular shape, reduction, explanation and approximate concepts", *Synthese* 111 (1997), 231-251; Eric R. Scerri "Bibliography on philosophy of chemistry", *Synthese*, 111 (1997), 305-324; Eric R. Scerri and L. McIntyre, "The case for philosophy of chemistry", *Synthese*, 111 (1997), 213-232; H. Vermeeren, "Controversies and existence claims in chemistry: the theory of resonance", *Synthese,* 69 (1986), 273-290; A.I. Woody, "Putting quantum mechanics to work in chemistry: the power of diagrammatic representations", *Philosophy of Science* (Proceedings), 67 (2000), S612-S627; R.G. Wooley, "The quantum interpretation of molecular structure", in Löwdin, Per-Olov, J.-L. Calais and O. Goscinski, eds., *Quantum chemistry – a scientific melting pot*, *International Journal of Quantum Chemistry* 12 Sup 1 (1978), pp. 307-13.

The story of quantum chemistry has been a story with a happy ending. A happy ending, however, of a tortuous journey. The beginning of which was marked by a self negating realization: that there could be no analytical solutions to almost all the problems of chemistry by using quantum mechanics, though in most of the cases the relevant equation(s) could be written down. But, the nightmare was punctuated by a dream of a dream world. A single instrument, the electronic computer, promised a boundless frontier of numerical solutions of arbitrary exactness. With it however, as it often happens in dream worlds, came another realization: as the first pioneers were experiencing this new frontier, the attractions provided by the very instrument of salvation led many astray.

The genesis and development of quantum chemistry as an autonomous subdiscipline owed much to those scientists who were able to realize that "what had started as an extra bit of physics was going to become a central part of chemistry". It owed much to those that managed to escape successfully from the "thought forms of the physicist"[18] by implicitly or explicitly addressing issues such as the role of theory in chemistry, the methodological status of empirical observations and virtual experiments, helped to create a new space for chemists to go about practicing their discipline. The ability to "cross 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, mathematics, and later biology, became a prerequisite to be successful in borrowing techniques, appropriating concepts, devising new calculational methods and developing legitimizing 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 instrument, 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[19]. 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 characterized "in-between" disciplines emerging throughout the 20th century – the exploration of frontiers and the crossing of disciplinary boundaries, reinforced by the mediation of many new instruments.

[18] Charles Alfred Coulson, "Recent Developments in Valence Theory", *Pure and Applied Chemistry*, 24 (1970), 257-287, 259.

[19] See Carsten Reinhardt, *Shifting and Rearranging: Physical Methods and the Transformation of Modern Chemistry* (Sagamore Beach, Mass.: Science History Publications, 2006).