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**Quantum Interdisciplinarity  
Friedrich Hund and Early Quantum Chemistry**

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Helge Kragh

## **Quantum Interdisciplinarity: Friedrich Hund and Early Quantum Chemistry**

In an often quoted and deservedly famous – or rather, perhaps, infamous – statement from the introduction to one of his papers, Paul Dirac wrote in 1929 that "quantum mechanics is now almost complete ... [and] the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known."<sup>1</sup> According to Dirac's reductionist view, chemistry was then subsumed under the laws of physics, although he admitted that "the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." But in principle, on the fundamental level (the only one which Dirac cared about) chemistry was claimed to be reduced to physics and in this sense explained. This was shortly after quantum mechanics had first been applied to chemical problems, and to the problem of valence in particular, and the promising results of the then infant quantum chemistry was undoubtedly a factor in Dirac's optimistic view, which in somewhat more cautious terms was repeated by other physicists (including Max Born, Walther Heitler and John Van Vleck). The reductionism also implied a certain disciplinary imperialism, for if chemistry was now explained in terms of quantum physics, chemists could scarcely any longer claim to deal with fundamental aspects of nature, but would be relegated to their traditional experiments and to theoretical work determined by and subjugated the laws formulated by the almighty physicists.

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<sup>1</sup> P. A. M. Dirac, "Quantum mechanics of many-electron systems," *Proc. Roy. Soc. A*213 (1929), 714-33, on p. 714.

The rivalry and disciplinary tensions that quantum chemistry caused between the communities of physicists and chemists can be seen as the continuation of an old competition between the two sister sciences which goes back to the early 19th century and which have many aspects besides the question concerning the structure of atoms and molecules.<sup>2</sup> I shall however limit myself to mention this one aspect in my brief and highly selective sketch of the origin of quantum chemistry, which properly speaking started with Niels Bohr's attempt of 1913 to extend his quantum theory of the atom also to the constitution of simple molecules.<sup>3</sup> In the second part of his famous series of papers of that year Bohr tried heroically, but unsuccessfully, to account for the covalent bond in hydrogen and other molecules; in 1920 the Munich physicist Walther Kossel developed Bohrian atomic chemistry to what he claimed was a theory of valence forces, but neither it nor other attempts to create a quantum basis for chemical compounds were satisfactory. In fact, the covalent bond (in contradistinction to the ionic bond) seemed to defy the Bohr-Sommerfeld quantum theory and was thus properly speaking an anomaly, a serious problem for the theory, but somehow Bohr and the other quantum theoreticians managed to convince themselves that they could ignore the problem – which they did.

Atomic and molecular theory were as much topics of concern for chemists as for physicists, and during the period of the old quantum theory there existed a vital chemico-theoretical tradition with the aim of constructing atomic and molecular models that would meet the needs of chemistry, such as the covalent bond, the spatial structure of molecules, isomerism, and coordination compounds.<sup>4</sup> The most active and well-known members of this tradition were perhaps Nevill Sidgwick in England and Gilbert Lewis, Irving

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<sup>2</sup> M. J. Nye, "Physics and chemistry: commensurate or incommensurate sciences?" 205-24 in M. J. Nye, J. Richards and R. Stuewer, eds., *The Invention of Physical Science* (Boston: Kluwer, 1992)

<sup>3</sup> H. Kragh, "Chemical aspects of Bohr's 1913 theory," *Journal of Chemical Education* 54 (1977), 208-10; Kragh, "Bohr's atomic theory and the chemists, 1913-1925," *Rivista della Storia Scienza* 2 (1986), 464-86.

<sup>4</sup> W. G. Palmer, *A History of the Concept of Valency to 1930* (Cambridge: Cambridge University Press, 1965). A. N. Stranges, *Electrons and Valence: Development of the Theory 1900-1925* (College Station, TX: Texas A&M University Press, 1982).

Langmuir and Albert Noyes from the United States. What matters here is that although the chemical atomic architects often paid lip service to the quantum theory and Bohr's atom, in reality their models were entirely different from the physicists' models and simply inconsistent with what was accepted as sound physical knowledge. This feature stands out most clearly and importantly in the case of valency, where the chemists favoured a static atom of the kind suggested by Lewis, where a shared pair of fixed electrons constitutes the valence bond; this was however a concept starkly contradicting the physicists' dynamic atom, for according to the physicists it was plain nonsense to fix orbital electrons in space – the atoms would collapse. Several chemists tried to reconcile the physical and chemical atomic theories, for example by picturing the covalent bond as one or two electrons orbiting elliptically around the two atomic kernels, but the pictures they constructed had no basis in physical theory and the claimed reconciliation was an illusion.

Just before quantum mechanics, the situation was thus that there existed two incompatible kinds of atomic models: on the one hand the physicists' dynamic quantum atom, which made physical sense but was largely impotent in matters of structural chemistry; and, on the other, the chemists' static models, which were highly successful in providing heuristics and qualitative chemical understanding, but were primitive and in fact impossible from a physical point of view. The result was that many physicists considered their chemical colleagues with little respect, or simply ignored them, and that many chemists considered their physical colleagues with equal disrespect, as theoreticians from another planet from whom nothing chemically useful could be expected.

The advent of quantum mechanics at first tended to aggravate this situation of mutual distrust, for not only was the new theory incomprehensible to most chemists because of its mathematical complexity, it also seemed to share its predecessor's impotence with regard to chemical applications. Few chemists would have understood the complicated calculations made by the Danish physicist Øyvind Burrau when he first solved the Schrödinger equation for the simplest possible chemical system, the normal state of the  $H_2^+$  ion, in 1926;<sup>5</sup> and if they did, they would not have been impressed by the chemical

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<sup>5</sup> Ø. Burrau, "Berechnung des Energieeigenwertes des Wasserstoffmolekel-ion ( $H_2^+$ ) im Normalzustand," *Kgl. Da. Vid. Selsk. Mat.-Fys. Medd.* 7, no. 14 (1927). J. Mehra and H.

usefulness of the calculations. And yet not all chemists looked to quantum mechanics with skepticism or lack of interest. In an important book on the electronic theory of valency completed in late 1926 Sidgwick urged his fellow-chemists to assimilate the new quantum theory and, as he wrote, "avoid ... the introduction of any physical hypotheses which are not already sanctioned by those who are best qualified to judge them."<sup>6</sup> In other words, Sidgwick accepted that there could be no such thing as a chemical atomic model distinct from the physical one, and in a sense he thus admitted the superiority of physics over chemistry as far as fundamental questions were concerned.

It was, at any rate, physicists and not chemists who laid the ground for quantum chemistry in 1927, first with the seminal work of Walther Heitler and Fritz London, who relied upon Heisenberg's slightly earlier resonance theory and developed it into a theory of the covalent bond which gave promising agreement with experiment when applied to the hydrogen molecule, namely a binding energy of two-thirds of the one found experimentally. The basic approach of Heitler and London was to consider separately one of the electrons in each of the combining atoms and then, by clever use of the Rayleigh-Ritz variation principle, to construct a wave function representing the paired-electron bond between them. The Heitler-London approach eventually became known as the valence bond (VB) method and became quickly the dominating method in prewar quantum chemistry, especially after it was developed into more manageable, more powerful and more applicable versions by Linus Pauling and John Slater.

This first breakthrough in quantum chemistry was clearly the work of physicists working within the culture of theoretical avant garde physics and with almost no knowledge of or concern about problems of structural chemistry. London had a dual background in philosophy and physics, and although Heitler had an interest in chemistry and did his Ph.D. work in the theory of solutions, he knew very little ordinary chemistry. In fact, neither Heitler and London nor other quantum physicists seem at first to have considered the covalent bond a crucial problem; in the spring of 1927 Heitler and London did not cooperate in order to solve this problem, but their aim was to understand the nature of the van der Waal forces between two hydrogen

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Rechenberg, *The Historical Development of Quantum Theory*, 5:2 (Berlin: Springer-Verlag, 1987), 850-55.

<sup>6</sup> N. V. Sidgwick, *The Electronic Theory of Valence* (Oxford, 1927), preface.

molecules; it was during their efforts to solve this problem that they happened to realize the role of exchange forces and then were led to suggest a mechanism for the chemical bond – an area very different from the one they had started out from.<sup>7</sup>

The same story – the indirect and unintentional way to approaching the valence problem – also holds good for the alternative method of quantum chemistry developed at about the same time, the molecular orbital (MO) method. This is the line of development in which Friedrich Hund made his most important marks and I shall therefore deal with it, and Hund's contributions in particular, in some more detail. The concept of molecular orbitals is commonly, and correctly, ascribed jointly to Hund and his American colleague Robert Mulliken, whose works in the late 1920s were tightly connected and followed parallel paths. They both took their departure in attempts to understand molecular spectra and were not at first interested in explaining the chemical bond, which was a result that grew out of their spectral works in a way neither of them had planned or foreseen. It is really impossible to deal with Hund's contributions in isolation from Mulliken's, so let me start with introducing Mulliken, who was born the same year as Hund, in 1896, but contrary to Hund and most other of the quantum chemical pioneers had a solid chemical training. After a Ph.D. in physical chemistry (at the University of University) he turned to the spectra of molecules and in 1925 we find him on his European pilgrimage and the first of several visits to Göttingen. It was on this occasion that he first met Hund, at the time still an assistant of Max Born's. Mulliken's efforts toward a better understanding of the structure of band spectra led him to try understanding also the molecular electronic states, and to conceive of them more or less in analogy with the electronic states of atoms. This was also the programme of Hund and so it is natural that the two had much to talk about when Mulliken again met him in the summer of 1927, on his next tour to Europe.

Friedrich Hund's background and approach were rather different from Mulliken's, but the differences in no way prevented a very fruitful exchange of ideas over the next years, sometimes directly by discussions or letters, more

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<sup>7</sup> K. Gavroglu and A. Simoes, "The Americans, the Germans and the beginnings of quantum chemistry," *HSPS* 25 (1994), 47-111, on p. 62. K. Gavroglu, *Fritz London: A Scientific Biography* (Cambridge: Cambridge University Press, 1995).

often indirectly by way of their various publications which had an inspiring effect on both of them and appeared as were they somehow coordinated – which they were not. The two scientists shared more than their age and an interest in molecular spectra; their ways of writing have also much in common – which is not to be taken as a compliment. Neither Hund nor Mulliken mastered the clarity and pointedness of presentation that characterize many of Pauling's papers. On the contrary, their papers are difficult to read and understand because they do not distinguish between crucial points and minor details, and many readers must have felt it difficult to see the wood – the message – because of all the trees in the shape of spectroscopic details in an often confusing notation. Most scientists end their papers with a conclusion where they sum up the main findings, but this was a pedagogic technique that Hund rarely used.

Mulliken, who at the time was assistant professor of physics, later described himself as "neither a proper experimentalist nor a proper theorist, but a middleman between experiment and theory – and between chemistry and physics."<sup>8</sup> This interdisciplinarity and pragmatism became a characteristic feature of the American approach to molecular science and quantum mechanics – the Americanization of molecular physics, as it has been called<sup>9</sup> – but it's a characteristic that doesn't fit at all on Hund, who in this respect was very much a representative of a central-European education and approach to physics.

Hund was a product of the Göttingen school, with its emphasis on theory and mathematical methods; he was an expert in the old Bohr-Sommerfeld quantum theory and quickly absorbed the new quantum mechanics and applied it to the study of molecules – and he was one of those who in the late 1920s introduced the "Gruppenpest," the application of group theory in quantum chemistry which so many less mathematically inclined physicists and chemists found unintelligible and plainly horrible. As to chemistry, Hund was an outsider, if not an ignorant. In an interview of 1963, Thomas Kuhn asked him why he didn't address valency in his early papers, and Hund said: "Ich schemte mich etwas, weil ich furchtbar wenig Chemie

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<sup>8</sup> R. S. Mulliken, "Molecular scientists and molecular science: some reminiscences," *Journal of Chemical Physics* 43 (1965), S2-SS11.

<sup>9</sup> A. Assmus, "The Americanization of molecular physics," *HSPS* 23 (1993), 1-33.

konnte. Ich hab' nie Chemie studiert und fühlte mich darum allen chemischen Fragen gegenüber unsicher und war darum vorsichtig."<sup>10</sup>

All the same, to all students of chemistry Hund's name is known from the rule that the build-up of electronic orbits take place in such a way that as many different orbits as possible are filled out with unpaired electrons before pairing in one orbit with opposite spins. Relying on the recently introduced Pauli principle, Hund formulated this rule in 1925, within the framework of the old quantum theory and without referring to spin explicitly.<sup>11</sup> Recall that the spin quantum number was only suggested by Goudschmidt and Uhlenbeck in the late summer of 1925 and that Pauli's famous exclusion principle was formulated without knowledge of spin. What today is generally known as "Hund's rule" was in the 1925 paper referred to as the "rule of maximum multiplicity" and was thoroughly hidden in spectroscopic details and terminology. It was of course formulated in a way very different from the modern textbook version, and it takes in fact some effort and reconstruction to recognize Hund's rule in his paper.

Hund first applied Heisenberg's new quantum mechanics to molecules in a paper completed in March 1926 and which appeared in print half a year later. "Zur Deutung einiger Erscheinungen in den Molekelspektren," as the title read, was the first in a long sequel of papers in which he developed his approach to quantum chemistry. In that paper, Hund introduced electron spin explicitly into band structure, which was shortly after the controversial concept had been understood in quantum mechanical terms and thus had become a legitimate part of quantum theory; it is also in this paper that we find, if only briefly and sketchily, the germ of the concept of molecular orbitals and the united-atom approach which became a hallmark of his and Mulliken's later work. Hund's approach was, essentially, to consider a diatomic molecule in its two most extreme (and unrealistic) states, one in which the atoms are completely separated and the other in which they are completely united into a single atomic system, and then find the intermediate distance at which the atomic spectroscopic terms coincide with the molecular ones. An adiabatic transition between the two extreme states is forbidden according to the Bohr-Sommerfeld theory, but Hund showed that in quantum mechanics it was a

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<sup>10</sup> AHQP interview, June 26, 1963. (Niels Bohr Archive).

<sup>11</sup> F. Hund, "Zur Deutung verwickelter Spektren, I," *Zs. Phys.* 33 (1925), 345-71.

legitimate and solvable procedure and that it allowed inferring the electronic states of simple molecules.

Hund's theory made a great impression on Mulliken, who saw in it a legitimation of his own, more phenomenologically based systematization of band spectra, and who in October 1926 wrote in a letter that "Hund really has *everything* in his paper. It's most remarkable. Nature of electronic states and fine structure both ... almost all of my conclusions seem to agree with his theory."<sup>12</sup>

At that time, the fall of 1926, Hund had completed his comprehensive work on atomic line spectra<sup>13</sup> and decided that the topic was well understood and no longer posed problems of a fundamental nature; with his background it was natural to seek new challenges in the area of molecular spectra and, if possible, to try explaining these in analogy with the theory of atomic spectra. He pursued this programme consistently during the next five years, first at Bohr's institute in Copenhagen where he spent the period from October 1926 to March 1927 on an International Educational Board fellowship. In Copenhagen Hund shared room with two of Bohr's Scandinavian associates, the Swede Oskar Klein and the Norwegian Svein Rosseland, and other visitors to the institute included Werner Heisenberg, Paul Dirac and Walther Heitler. It was here he prepared part I and II of the important series of papers with the common title "Zur Deutung der Molekelspektren" which appeared in five parts in the *Zeitschrift für Physik* between 1927 and 1930.

When Hund studied Schrödinger's new wave mechanics in the spring and summer of 1926, at first he didn't like it and found it to be a formal calculational scheme – a reaction not untypical for physicists educated in the Göttingen tradition; but he soon realized that it was a very useful scheme and first applied wave mechanics to molecular spectra in part I of "Zur Deutung der Molekelspektren" which was completed in November. Although Hund concentrated on the theory of molecular spectra, apparently he also felt tempted to apply the Schrödinger equation to simple molecules in a more direct way, that is, to treat them as eigenvalue problems. This is suggested by a letter from Heisenberg to Pauli of November 23, 1926, in which Heisenberg reported that "Das  $H_2^+$  hat Hund den Herrn Burrau hier überlassen und der

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<sup>12</sup> Mulliken to R. T. Birge, 17 Oct 1926, quoted in Gavroglu & Simoes, p. 54

<sup>13</sup> F. Hund, *Linienpektren und Periodisches System der Elemente* (Berlin: J. Springer, 1927)

hat es nun wirklich endgültig in Ordnung gebracht," a sentence which I take to imply that Hund and Burrau were both interested in taking on the problem, but that they agreed to leave it to Burrau rather than duplicating work or write a joint paper.<sup>14</sup> Burrau had at that time worked with the problem for several months and so it was reasonable that Hund agreed to let him complete the calculations.

As mentioned, Mulliken worked more or less parallelly with Hund, and in the summer of 1928 he (Mulliken) published an important paper in which he introduced the concept of "promoted electrons" and systematized the simplest molecular spectra by assigning quantum numbers to the individual electrons in a molecule. Hund had arrived at some of the same results and had just submitted his manuscript to the editor of the *Zeitschrift* when he received a copy of Mulliken's paper, which made him withdraw his manuscript, send a copy of it to Mulliken, and write a new one which combined Mulliken's and his own ideas.<sup>15</sup> It was in these two works of 1928 that the molecular orbital method was first expounded, although still in a molecular-spectrum context and without explicit application to the chemical bond. A basic feature in what may be called the Hund-Mulliken theory was their heuristic use of the so-called *Aufbauprinzip* (or construction principle), which was originally formulated by Bohr in a rather different context, namely in his 1922 atomic theory of the periodic system;<sup>16</sup> according to Bohr the building-up of atomic orbits could be understood by a hypothetical series of successive captures of electrons in the lowest available energy state, starting with hydrogen and ending with uranium, and Hund and Mulliken independently made use of a similar, but molecular *Aufbauprinzip* for diatomic molecules. But whereas Mulliken started with the molecular spectra and from these derived electronic configurations, the more theoretically oriented Hund took a deductive approach by formulating a general, molecular *Aufbauprinzip* and then compare its results with those suggested by known spectra.

Hund was thoroughly familiar with Bohr's old and by 1928 obsolete theory of the periodic system, which also acted as a strong inspiration for Mulliken, who used Bohr's principle in a more visual way than Hund. Much

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<sup>14</sup> Pauli Briefwechsel I, p. 359

<sup>15</sup> F. Hund, "Recollections of Robert S. Mulliken," vii-x in R. S. Mulliken, *Life of a Scientist* (Berlin: Springer, 1968).

<sup>16</sup> H. Kragh, "Bohr's second atomic theory," *HSPS* 10 (1979), 123-86.

later, Mulliken recalled that "Bohr's Aufbauprinzip made a very great impression on me and so I thought something similar for molecules would be nice. If you translate orbits into orbitals for atoms, then for molecules it is molecular orbitals; it is something that goes around all the atoms or however many atoms there are and the Aufbauprinzip transferred to molecules simply means molecular orbitals."<sup>17</sup> However, whereas it was essential in Bohr's original use of the Aufbauprinzip that the quantum numbers didn't change during the capture process, Mulliken and Hund – who contrary to Bohr were equipped with the Pauli principle – realized that in the formation of molecules some electrons could have their value of the principal quantum number increased in the process, which was what Mulliken referred to as promoted electrons.

From a methodological point of view Hund's and Mulliken's 1928 papers were strikingly different in their attitude to quantum mechanics, which reflected a general difference between American and German styles in physics. Hund manoeuvred confidently with abstract quantum mechanics, but Mulliken's work was essentially based on the old quantum theory and he simply did not use the Schrödinger equation or other of the apparatus of quantum mechanics; not only was he able to obtain important results without using quantum mechanics, the Bohr-Sommerfeld theory also appealed to him because he could then better visualize the molecular orbitals in analogy with the electron orbits of the old theory. His attitude to the new quantum mechanics was entirely pragmatic and, as he later recalled, "I was more interested in getting better acquainted with molecules than with abstract theory about them."<sup>18</sup> To Hund, on the other hand, quantum theory was more interesting than molecules, and he didn't quite appreciate the eclectic and pragmatic approach of his American colleague. In a letter to London from the summer of 1928 he made the following comment on Mulliken's new paper: "[It] is rather American, that is, he proceeds by groping in an uncertain manner, where one can say theoretically the cases for which a particular claim is valid."<sup>19</sup>

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<sup>17</sup> AHQP interview with Mulliken; Gavroglu & Simoes, p. 55.

<sup>18</sup> Mulliken, *Life of a Scientist*, p. 59.

<sup>19</sup> Hund to London, 13 Jul 1928 (Gavroglu & Simoes, p. 108).

In 1928 the molecular orbital method had been formulated, but it was not yet conceived as a method of explaining the chemical bond and the works of Hund and Mulliken were therefore not clearly seen as an alternative to the valence bond method of Heitler, London and Pauling. It gradually became so between 1928 and 1931, when Hund and Mulliken began to turn their interest toward valency and when other physicists, in particular Gerhard Herzberg in 1929, used methods closely related to the molecular-orbital method in studies of chemical bonding and in predicting the stability of molecules.<sup>20</sup> Herzberg explained the chemical bond within the Hund-Mulliken framework by introducing not only bonding but also antibonding electrons which could counteract the bonding electrons.

The molecular orbital method as a valence theory reached maturity in 1931 when Mulliken and Hund in separate papers developed the molecular orbital theory into a new bonding theory alternative to the valence bond theory which they both found objectionable. In his "Zur Frage der chemischen Bindung" Hund demonstrated the power of the method by treating the tetrahedral bonds of carbon and also the benzene molecule, thereby duplicating slightly earlier work by Pauling and Erich Hückel, respectively, where Pauling used the valence bond method and Hückel the molecular orbital method. Hückel's important work on aromatic compounds was his Habilitationsschrift as lecturer in theoretical physics at the Stuttgart Technische Hochschule and was in part indebted to Hund with whom he had discussed it.

By 1931 quantum chemistry was developed to a high level, fundamentally the theory we have today, but it was only beginning to percolate into chemistry from its origins in quantum theory and molecular physics, and more slowly in the case of the molecular orbital than the valence bond method. This is not surprising, perhaps, for the latter method started from the assumption that the chemical bond depends on interaction between complete atoms, and this was close to the chemists' traditional point of view such as included in the Lewis picture of shared electrons. In fact, the valence bond method was often seen as a sophisticated quantum version of Lewis' qualitative model. The Hund-Mulliken theory, on the other hand, was in a sense more radical, more strange from a chemical perspective, for it was based on quantum mechanical interaction between all the atomic nuclei and all the

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<sup>20</sup> P. Villadsen, "Teorier for den kemiske binding" (unpubl. thesis, Aarhus University, 1988).

electrons of a molecule. The electronic configuration of the hydrogen molecule, for example, was not treated as if the molecule was composed from two atoms, but by considering hydrogen as if it were derived from a fission of helium – surely a line of thinking unfamiliar to chemists. It is somewhat remarkable that Mulliken – the only of the quantum chemical pioneers with a sound background in chemistry – in a review paper of 1935 described the Heitler-London method as "[following] the ideology of chemists," whereas his own and Hund's method "treats each molecule, so far as possible, as a unit."<sup>21</sup>

It is noteworthy that all the founding papers in quantum chemistry, whether belonging to the valence bond or the molecular orbital tradition, were published in physics journals in Germany and the United States and that even Mulliken, trained as a chemist, addressed his important works to physicists rather than chemists. Hund published invariably in *Zeitschrift für Physik* and until 1929 Mulliken's papers appeared in *Proceedings of the National Academy of Science*, *Physical Review* or *Reviews of Modern Physics*. But of course quantum chemistry was as much the concern of chemists as of physicists, and with Pauling's entry on the scene a marked shift toward the chemical community took place, culminating with Pauling's influential series of papers on "The nature of the chemical bond" which appeared from 1931 in the *Journal of the American Chemical Society*.<sup>22</sup> Also Mulliken turned to the chemical audience, first in a review paper of 1929, but Hund continued to publish in the *Zeitschrift für Physik* or, in one case, the *Zeitschrift für Astrophysik*. There seems to have been a less fruitful contact between German physicists and chemists than between their American counterparts, and at any rate Hund didn't feel at home with chemical traditions and culture. He did however address chemical audiences a few times, first at the 1928 annual meeting of the *Bunsen Gesellschaft* in Munich, where he had the opportunity to discuss matters with London (BG = German Society for Electrochemistry and applied Physical Chemistry). The following year he participated in a meeting of the *Faraday Society* in London, where Heitler, Fritz London, and Lennard-Jones

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<sup>21</sup> Gavroglu, *Fritz London*, p. 81.

<sup>22</sup> Y. Abe, "Pauling's revolutionary role in the development of quantum chemistry," *Historia Scientiarum* 20 (1981), 107-24.

were present, and he also attended the Bunsen Gesellschaft's meeting in Heidelberg in 1930, when he and Mulliken were invited to give lectures.<sup>23</sup>

The German quantum physicists' arrogance and lack of respect for the chemists may be glimpsed from a letter of Fritz London to Heitler of 1935, where London says that the chemist's concept of valence is designed as a substitute for thinking and complicated calculations and where he ends saying that "the chemist is made out of hard wood and he needs to have rules even if they are incomprehensible."<sup>24</sup> Something of the same attitude is part of Hund's reply of 1963 to Kuhn's question of how the chemists reacted to the new ideas. I quote from Hund's reply: "Die Chemiker waren natürlich mit Einzelfragen beschäftigt, die kannten ja das periodische System und den Valenzbegriff, und damit waren sie ja Zufrieden. ... Aber die Chemiker konnten natürlich nicht die Quantentheorie verstehen."<sup>25</sup>

In spite of the successes of the Hund-Mulliken molecular orbital approach, it was the Heitler-London-Pauling valence bond method with its emphasis on resonance which dominated quantum chemistry in the 1930s. I cannot go into this development and shall suffice to mention that the molecular orbital method experienced a strong comeback after the war when Mulliken, Charles Coulson, John Lennard-Jones and others argued that it could be applied to complicated molecules more easily and more generally than the valence bond alternative. Among the official recognitions was the Nobel prize awarded in 1966 to Mulliken for his "fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method." In his acceptance speech in Stockholm, Mulliken modestly argued that the method for which he was awarded the price was in reality the work of many researchers and he stressed in particular "the major contribution of Professor Hund in its early development."<sup>26</sup>

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<sup>23</sup> F. Hund, "Quantenmechanik und chemische Bindung," *Zs. Electrochemie* 34 (1928), 437-42; "Chemical binding," *Trans. Faraday Soc.* 25 (1929), 646-48; "Methoden der Deutung und Vorhersage von Molekelspektren," *Zs. Elektrochemie* 36 (1930), 565-828.

<sup>24</sup> Gavroglu & Simoes, p. 101.

<sup>25</sup> AHQP interview.

<sup>26</sup> R. S. Mulliken, "Spectroscopy, molecular orbitals, and chemical bonding," pp. 131-59 in *Nobel Lectures. Chemistry 1963-1970* (Amsterdam: Elsevier, 1972).

I want to conclude with some more general comments on the two mentioned methods of quantum chemistry, the valence bond and the molecular orbital method. Before doing that, let me add that my account of the origin of the molecular orbital method has of course been incomplete and selective, and that Hund and Mulliken were not after all the only scientists responsible for the method. I have already mentioned the contributions of Herzberg and Hückel, and a more careful account would include in somewhat minor roles Lennard-Jones in England, Edward Condon in the United States, and probably a few others, but it is significant that the formative phase of quantum chemistry was entirely dominated by German and American scientists; some contributions came from British physicists, but (with the exception of Burrau's early paper) I am not aware of a single major work from other countries. The European centre of quantum chemistry shifted from Germany to England during the 1930s and at the same time the United States evolved as the unchallenged world leader in the field.

Without going in detail it is rather evident that the political situation in Germany after 1933 had a great deal of the responsibility for the change, but it is also important to be aware that the American hegemony in the 1930s was far from based on German refugee physicists; in fact, Fritz London was one of the few German pioneers in quantum chemistry who came to America. The American strength is rather to be found in the cultivation of interdisciplinary work in physical chemistry and chemical physics which goes back to the early 1920s, when there already existed a strong American tradition in molecular quantum physics, headed by scientists such as Edwin Kemble and Raymond Birge, and the next generation of which counted Van Vleck, Edward Condon, Philip Morse, David Dennison and Mulliken. These scientists originally focused on band spectra but soon extended their domain to cover also other areas of atomic and molecular physics, and by the 1930s they had developed it into a new interdisciplinary subfield, chemical physics – an American invention which differed from both pure quantum chemistry and traditional physical chemistry. Contributing to the American success was probably also the pragmatic American style and instrumentalist attitude to quantum physics which were so excellently suited to the new kind of applied quantum chemistry.<sup>27</sup>

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<sup>27</sup> S. S. Schweber, "The young John Slater and the development of quantum chemistry," *HSPS* 20 (1990), 339-406.

The two methods of chemical bonding competed for several decades in a sort of controversy with Mulliken as the chief spokesman for molecular orbitals and Pauling and others arguing the cause of valence bonds – Hund doesn't seem to have been much interested in this discussion which concerned chemistry more than physics. Rather than speaking of two completely different theories, we should probably think of the rival methods as supplementary research programmes which emphasized different points and had their respective strengths and weaknesses, but none of which can claim to be the one and only correct theory of molecules. They are both good models, but they only give partial truths and explain a selection of data. This, in fact, seems to be the way most chemists thought about the two approaches, and much of the heat of the controversy was rhetorical, apparent rather than substantial. It was increasingly realized that complex systems like chemical compounds cannot be fully explained by a single physical model and that an eclectic use of both or more methods may be the only way to progress – in Bohr's terminology one may say that they are complementary.

To return to the quotation of Dirac, with which I started, one may say that although he may have been right in principle, then principles don't count much for chemists, and theoretical chemistry is still today a rather messy, semi-empirical science based upon a Schrödinger equation that can hardly ever be solved. More importantly, the physicists' dream (and the chemists' nightmare) of reducing chemistry to quantum physics seems to belong to exactly the world of dreams. Philosophers and scientists have argued that molecular structures cannot, not even in principle, be reduced to a matter of quantum mechanics and that there is an important difference between an isolated physical molecule and the real, chemical molecules.<sup>28</sup> Whatever the answer to this philosophical discussion about reductionism, it is a historical fact that although quantum mechanics provided chemistry with a new understanding, in reality this understanding depended heavily upon purely chemical facts. Quantum chemistry was not founded on physics alone, and even less on quantum mechanics alone, although this was what it may have looked like at the time Dirac wrote his statement; but the development during the 1930s clearly showed that physical theory alone was insufficient and that the classical attitude of physics was in fact a hindrance to progress in quantum chemistry.

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<sup>28</sup> H. Primas, *Chemistry, Quantum Mechanics, and Reductionism* (New York: Springer, 1981).

The American and British quantum chemists of the 1930s mastered the methods of quantum mechanics, but they now had to reeducate themselves in order to escape the thought-forms of physicists and create a new disciplinary framework which borrowed from, but was not dominated by, physics.

Finally, it may be interesting to compare the two classical molecular methods also from a more philosophical point of view, for they were research programmes differing not only with regard to heuristics, fruitfulness and predictive power, but also in their associated ontology and metaphysics. Thus it has been argued that the valence bond method relates to positivistic and reductionist standards in the sense that a molecule is conceived as a sum of atoms plus valence bonds; the wave function is a mixture of two or more states and in the case of resonating structures, such as in the benzene molecule, there is no way to tell what structure is really present, or, in general, what state an electron is in. This is a situation reminding of the Schrödinger cat paradox, and its interpretation according to the valence bond picture seems to agree nicely with the Copenhagen interpretation of quantum mechanics where it is meaningless to speak of the reality of non-observed systems. Incidentally, it was this kind of considerations which for a period in the 1940s made valence bonds and resonance structures politically incorrect concepts in the Soviet Union. The molecular orbital method, on the other hand, is holistic rather than reductionistic and permits a more realist interpretation. Mulliken often emphasized what he called the "molecular point of view," namely that the molecular orbital method gives ontological priority to the molecule as such; it is not necessary to think of valence bonds as existing in the molecule; all there is is a wavefunction representing the distribution of electrons each of which is assigned definite quantum numbers and thus a particular state, although that state may be spread out over the entire molecule.

As I hope I have demonstrated, quantum chemistry has a history which is rich and interesting and one which may even provide food for thought for philosophers of science.<sup>29</sup> It is only recently that a few scholarly works on early quantum chemistry have appeared, most notably by Sam Schweber, Yuko Abe, Kostas Govraglu and Ana Simoes, but in general

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<sup>29</sup> D. A. Bantz, "The structure of discovery: evolution of structural accounts of chemical bonding," pp. 291-329 in T. Nickles, ed., *Scientific Discovery: Case Studies* (Dordrecht: Reidel, 1983).

historians of modern physics and chemistry have avoided the field which is clearly in an underdeveloped state compared with the history of many other branches of modern science. I tend to believe that the relative lack of interest in the development of this great and unexplored area of modern science is in part a result of its uncomfortable location between the classical disciplines of physics and chemistry; yet it is not least the interdisciplinarity which makes quantum chemistry a fascinating topic to study in a historical perspective.