

# 1 Quantum Chemistry *qua* Physics: The Promises and Deadlocks of Using First Principles

In the opening paragraph of his 1929 paper “Quantum Mechanics of Many-Electron Systems,” Paul Adrien Maurice Dirac announced that:

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. (Dirac 1929, 714, emphasis ours)

For most members of the community of physicists, it appeared that the solution of chemical problems amounted to no more than quantum-mechanical calculations. Physicists came under the spell of Dirac’s reductionist program, and quantum chemistry came to be usually regarded as a success story of quantum mechanics. Although it took some time for physicists to realize that Dirac’s statement was a theoretically correct but practically meaningless dictum, the first attempts to solve chemical problems in the “proper way”—that is, in the physicists’ way—appeared to be rather promising. These attempts started before the publication of Dirac’s paper, and they may have provided some kind of justification for such a generalized statement.

## The Old Quantum Chemistry: Bonds for Physicists and Chemists

The prehistory of quantum chemistry has its beginnings in the 1910s with various attempts, both by physicists and chemists, to explain the nature of bonds within two essentially disparate theoretical traditions—physical chemistry and molecular

spectroscopy—and two conflicting views of atomic constitution. For Gilbert Newton Lewis, the emblematic albeit idiosyncratic representative of the first group, the starting point was the static atom of the chemists. For Niels Bohr whose views were closer to those of the second tradition, the starting point was his dynamical atom, soon appropriated by the physicists and used to explain the complexities of molecular spectra.

In the last part of his trilogy “On the Constitution of Atoms and Molecules,” Bohr considered systems containing several nuclei and suggested that most of the electrons must be arranged around each nucleus in such a way “as if the other nucleus were absent.” Only a small number of the outer electrons would be arranged differently, and they would be rotating in a ring around the line connecting the nuclei. This ring, which “keeps the system together, represents the chemical ‘bond’” (Bohr 1913, 862).<sup>1</sup> According to these general guidelines, in the hydrogen molecule the two electrons were rotating in a ring in a plane perpendicular to the line joining the nuclei. Although Bohr tentatively suggested a model for the water molecule,<sup>2</sup> it was in the case of the hydrogen molecule that he ventured to prove quantitatively its mechanical stability, offering a value for the molecular heat of formation twice as large as the experimental one (Langmuir 1912). Thus, the chemical consequences of Bohr’s molecular model conflicted with experimental data for the simplest molecule, and the calculations were much too complicated to be carried through in the case of more complex molecules.

The exploration of another molecular model—the Lewis model with the shared electron pair, a topic we address in chapter 2—was, however, to give a satisfactory, albeit qualitative, answer to the problem of chemical bonding. The translatability of Lewis’s picture into Bohr’s dynamical language was found by “transforming” Lewis’s static shared electrons into orbital electrons revolving in *binuclear* trajectories (Kemble et al. 1926). In the simplest case of diatomic molecules, and reasoning by analogy with the hydrogen molecule, the binding orbits of shared electrons were thought to fall into two distinct classes. In the class most directly associated with the Lewis model, shared orbital electrons were thought to move in binuclear orbits around both nuclei, providing the necessary interatomic binding “glue” on the assumption that electrons spent most of their time in the region between nuclei. In the second class, following Bohr’s suggestion, shared electrons moved either in a plane perpendicular to the line joining the two nuclei or in crossed orbits. Similar models were explored in the case of the hydrogen molecule ion with the difference that only one electron was involved (Pauli 1922).

Again, agreement with experimental values for the few cases where quantitative calculations could be carried on could not be achieved.

Quite independently from considerations related to atomic spectroscopy, quantization was applied to molecules 2 years before it was applied to atoms (Jammer 1966;

Kuhn 1978; Hiebert 1983; Barkan 1999). But whereas Bohr's revolutionary assumption related radiation frequencies to energy changes accompanying electronic jumps between allowed orbits, in the case of the molecule, the more conservative Niels Bjerrum (a physical chemist and compatriot and friend of Bohr) accepted the classical electrodynamical identity between the frequency of emitted radiation and the mechanical frequency of motion. His hybrid model assumed simply the quantization of rotational energy, in conjunction with classical electrodynamics and the equipartition theorem. Starting with a simple model of the molecule as a vibrating rotator, Bjerrum provided a model to explain the infrared molecular spectra of some simple diatomic molecules and confirmed the long-sought interdependence between kinetic theory and spectroscopy within the framework of a very "restricted" quantum theory.

The close agreement between theory and experiment provided a strong argument in favor of quantization of rotational energies/frequencies. Such was the opinion of Bohr in a letter to Carl W. Oseen: "I do not know what your point of view of the quantum theory really is; but to me it seems that its experimental reality can hardly be doubted, this is perhaps most evident from Bjerrum's beautiful theory, and Eva von Bahr's papers almost seem to offer direct proof of the quantum laws or at least of the impossibility of treating the rotation of molecules with anything resembling ordinary mechanics."<sup>3</sup>

The interpretation of infrared molecular spectra proved to be so successful that atomic and molecular spectroscopy developed as quite separate branches until 1919–1920. Then, Torsten Heurlinger (a graduate student of Johannes Rydberg who held one of the chairs of experimental physics at the University of Lund) and Adolf Kratzer (Arnold Sommerfeld's former Ph.D. student and assistant), completing the work started by physicist Karl Schwarzschild, showed that Bohr's frequency condition could be extended beyond the motion of electrons and applied to the interpretation of the rotational and vibrational motions of molecules in such a way that Heurlinger and Kratzer managed to unite atomic and molecular spectroscopy under the same theoretical umbrella. The American physicist and expert on molecular spectra Edwin Crawford Kemble noted that the interpretation of band spectra by the Einstein–Bohr hypothesis that spectroscopic frequencies are the measures of energy differences and are not identical to the frequencies of the motion of the emitting system undermined the semiclassical theory of Bjerrum, despite its many successes. "The abandonment of the initially successful Bjerrum theory has been brought about primarily by the necessity of unifying our interpretation of line and band spectra" (Kemble et al. 1926, 107). From then on, spectroscopists calculated the frequencies of the emission/absorption in molecular spectra by using the quantization of energy *plus* the Einstein–Bohr frequency relation, now applied to all frequency regions, whether in the infrared, red, visible, or ultraviolet part of the electromagnetic spectrum.

## Walter Heitler and Fritz London: Outlining a Program for Quantum Chemistry

### The Heitler and London Paper of 1927

The stability of the hydrogen molecule within the newly developed quantum mechanics was first successfully explained by Walter Heitler and Fritz London in their paper of 1927 (Gavroglu and Simões 1994; Gavroglu 1995; Karachalios 2000).<sup>4</sup> In April of that year, Heitler and London, both recipients of a Rockefeller Fellowship, decided to go to the University of Zürich where Erwin Schrödinger was—they both felt more at ease with his more intuitive approach than with Werner Heisenberg's matrix mechanics. Schrödinger agreed to their stay, but there was not much collaboration with him.

Fritz London (1900–1954) was born in Breslau to a Jewish family. His father was professor of mathematics at the University of Breslau. In 1921, the year he graduated from the University of Munich, he wrote a thesis under the supervision of Alexander Pfänder (one of the best known phenomenologists) dealing with deductive systems. It was among the very first attempts to investigate ideas about philosophy of science expressed by the founder of the phenomenological movement in philosophy, Edmund Husserl. It was a remarkable piece of work by a 21-year-old who developed an anti-positivist and antireductionist view. In fact, London's first published paper in a professional journal was in philosophy. He published his thesis in 1923 in the *Jahrbuch für Philosophie und phänomenologische Forschung*, and Pfänder, along with Moritz Geiger and Max Scheler, was one of the co-editors of the *Jahrbuch*, whose editor in chief was Husserl himself. London first went to work with Max Born at the University of Göttingen, but Born could not dissuade him from working in philosophy and sent him to Arnold Sommerfeld at the University of Munich. He did his first calculations in spectroscopy, and, in 1925, he published his first paper in physics with H. Honl on the intensity of band spectra.

Concerning his approach to philosophy, London did not follow the practice of a lot of physicists who were either among the founders of quantum mechanics or among its first practitioners (Everitt and Fairbank 1973; Gavroglu 1995). Most of these physicists wrote some kind of a philosophical piece *after* having made those contributions by which they established their reputations in the community. Some of these pieces are texts for a rather sophisticated audience, but most are popularized accounts—explanations of the implications of quantum mechanics and relativity, historico-philosophical accounts of the development of what is called “modern physics,” attempts to present in a systematic manner a series of philosophical issues within the context of the new developments. London followed a different path. His work in philosophy, never mentioned by others when there is reference to the philosophical writings of this generation, was of the professional kind and was impressively ambitious: He wanted to discuss the status of a deductive theory and the conditions for the existence of such a theory. In a thoughtful essay examining Husserl's philosophy

of science, Thomas Mormann (1991) considers London's thesis together with Husserl's ideas concerning philosophy of science as having anticipated the semantic approach to the philosophy of science.

London's first academic appointment, starting in October 1925, was as Paul Peter Ewald's assistant at the Technische Hochschule in Stuttgart. Ewald was the director of the Institute for Theoretical Physics, and it was in this environment that London started working on quantum theory. In fact, instead of continuing to work in spectroscopy as the "Sommerfeld culture" stipulated, London, as soon as he reached Stuttgart, plunged into matrix mechanics. He first used Carl Gustav Jacob Jacobi's classical transformation theory of periodic systems and "adopted" it for matrix mechanics proving that energy conservation was independent of the combination principle of atomic theory. This he proved after showing that the two definitions of the matrix derivative in the famous "three-man paper" of Born, Heisenberg, and Pascual Jordan followed from his proposal of a more general definition of the matrix derivative (Jammer 1966; Hendry 1984; Kragh 1990).

His next two papers were quite significant in what came to be known as the transformation theory of quantum mechanics, a theory that was independently and much more fully developed and completed by Dirac and Jordan in 1926–1927. Eventually, transformation theory allowed quantum mechanics to be formulated in the language of Hilbert spaces. In this new framework, quantum mechanics could be treated in a mathematically more satisfactory way, and its results could acquire a consistent physical interpretation, dependent less on visualizability and on a description in space-time and giving more emphasis on underlining the novel foundational characteristics of quantum mechanics.

Walter Heitler (1904–1981) was born in Karlsruhe to a Jewish family, and his father was a professor of engineering. His interest in physical chemistry grew while he attended lectures on the subject at the Technische Hochschule, and through these lectures he came into contact with quantum theory. He had also acquired a strong background in mathematics. Wishing to work in theoretical physics, he first went to the Humboldt University of Berlin but found the atmosphere not too hospitable especially because a student was left to himself to choose a problem and write a thesis. Only after its completion would the "great men" examine it. After a year in Berlin he went to the University of Munich and completed his doctoral thesis with Karl Herzberg on concentrated solutions. The writing of his thesis coincided with the development of the new quantum mechanics, but because of the kind of problems he was working on, he never had the opportunity to study the new developments in any systematic manner. After completing his thesis, Sommerfeld helped him to secure funding from the International Education Board, and he went to the Institute for Theoretical Physics at Copenhagen to work with Bjerrum on a problem about ions in solutions. He was not particularly happy in Copenhagen. Determined to work in quantum mechanics,

he convinced Bjerrum, the International Education Board, and Schrödinger to spend the second half of the period for which he received funding in Zürich (Heitler 1967; Gavroglu 1995).

About a month after arriving in Zürich, Heitler and London decided to calculate the van der Waals forces arising from weak attractive interactions between two hydrogen atoms considering the problem to be “just a small ‘by the way’ problem.” Nothing indicates that London and Heitler were either given the problem of the hydrogen molecule by Schrödinger or that they had detailed talks with him about the paper. Linus Pauling, who was also in Zürich during the same time as Heitler and London, noted that neither he nor Heitler and London discussed their work with Schrödinger,<sup>5</sup> despite the fact that Schrödinger knew what they were all working on as witnessed by Robert Sanderson Mulliken’s visit to Zürich in 1927. Schrödinger (figure 1.1) told Mulliken that there were two persons working in his institute who had some results “which he thought would interest me very much; he then introduced me to Heitler and London whose paper on the chemical bond in hydrogen was published not long after” (Mulliken 1965, S7). Ewald thought that the question of the homopolar bond was in London’s mind before going to Zürich, and Pauling remembered discussions with Heitler about bonding when he was in Munich in 1926.



**Figure 1.1**

Erwin Schrödinger and Fritz London in Berlin in 1928.

Source: Courtesy of Edith London.

Heitler and London's initial aim was to calculate the interaction of the charges of two atoms "without even thinking of the exchange." They were not particularly encouraged by their result because the Coulomb integral, which represents the energy that an electron would have in the diatomic molecule if it occupied one atomic orbital, could not account for the van der Waals forces: "So we were really stuck and we were stuck for quite a while; we did not know what it meant and did not know what to do with it,"<sup>6</sup> Heitler remembered. Heisenberg's work on the quantum mechanical resonance phenomenon, which had already been published, was not of particular help to Heitler and London, as the exchange was part of the resonance of two electrons, one in the ground state and the other excited, but both in the same atom (Carson 1996).

Years later, Heitler would still remember the hot afternoon, "the picture before me of the two wave functions of two hydrogen atoms joined together with a plus and minus and with the exchange in it." He called London and they started to work on the idea, and by daybreak they had resolved the problem of the formation of the hydrogen molecule. They had also realized that there was a second type of interaction, a repulsive one between the two hydrogen atoms, something they were unaware of but that was nothing particularly new, as a number of chemists were aware of the old electrochemical hypothesis as to the nature of the chemical bond. And though they were able to complete the calculation, they had "to struggle with the proper formulation of the Pauli principle, which was not at that time available, and also the connection with spin . . . There was a great deal of discussion about the Pauli principle and how it could be interpreted."<sup>7</sup>

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

$$\Psi = c_1 \Psi_a(1) \Psi_b(2) + c_2 \Psi_a(2) \Psi_b(1).$$

The problem now was to calculate the coefficients  $c_1$  and  $c_2$ . This they did by minimizing the energy,

$$E = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau}.$$

They found two values for the energy,

$$E_1 = 2E_0 + \frac{C + A}{1 + S_{12}}; \quad E_2 = 2E_0 + \frac{C - A}{1 - S_{12}}.$$

$S_{12}$  is the overlap integral and measures the extent to which the two atomic wave functions overlap one another ( $\int \psi_a \psi_b d\tau$ ). The integral  $C$  is the Coulomb integral ( $\int \psi_a H \psi_a d\tau$ ), and  $A$  is the exchange integral ( $\int \psi_a H \psi_b d\tau$ ). Both  $C$  and  $A$  had negative

values, but  $A$  was larger than  $C$ .  $E_1$  implied  $c_1/c_2 = 1$ , and  $E_2$  implied  $c_1/c_2 = -1$ . Hence the wave function of the system could now be written as

$$\Psi_I = \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)$$

$$\Psi_{II} = \Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1).$$

Up to now, the spin of the electrons was not taken into consideration. The symmetry properties required by the Pauli exclusion principle were satisfied only by  $\Psi_I$ . This was the case when the electrons had antiparallel spins. But  $\Psi_I$  corresponded with  $E_1$ .  $E_1$  was less than  $2E_0$ , the sum of the energies of the two separate hydrogen atoms, and, hence, it signified attraction.  $\Psi_{II}$ , which when spin was taken into consideration was a symmetric combination, corresponded with  $E_2$ . But  $E_2$  was greater than  $2E_0$ , and it implied repulsion. The bonding between the two neutral hydrogen atoms became possible only when the relative orientations of the spins of the electrons were antiparallel. They noted that this was the justification for the electron pairing that Walter Kossel had talked about, but they did not refer to Gilbert Newton Lewis (Kohler 1971, 1973). To form an electron pair it did not suffice to have only energetically available electrons; they also had to have the right orientations. The homopolar bonding could, thus, be understood as a *pure quantum effect*, as its explanation depended wholly on the electron spin, which had no classical analogue. Heitler and London (1927, 472) found the energy to be 54.2 kcal/mole (2.4 eV/molecule) and the internuclear distance 0.8 Å.<sup>8</sup>

William M. Fairbank, who was London's colleague at Duke University in the early 1950s and the co-author with C. W. Francis Everitt of the entry on Fritz London in the *Dictionary of Scientific Biography*, recalled London telling him that Schrödinger was pleasantly surprised because he did not expect that his equation could be used to solve chemical problems as well. Born and James Franck were very enthusiastic about the paper. Sommerfeld had a rather cool reaction, but he also became very enthusiastic once Heitler met him and explained certain points.

The exchange force remained a mystery. Heitler and London were not expecting to find any such force, as London had told Alfred Brian Pippard, because they had started working on the problem as a problem in van der Waals forces.<sup>9</sup> They soon realized that the proposed exchange mechanism obliged them to be confronted with a fundamentally new phenomenon. They had to answer questions posed by experimental physicists and chemists about what was exchanged: Were the two electrons being *actually* exchanged? Was there any sense in asking what the frequency of exchange is? It was eventually realized by both that the exchange was a fundamentally new phenomenon with no classical analogue. "I think the only honest answer today is that the exchange is something typical of quantum mechanics, and should not be interpreted—or one should not try to interpret it—in terms of classical physics."<sup>10</sup> Both London and Heitler in all their early writings repeatedly stressed this "non visu-

alizability” of the exchange energy. It is one aspect of their work that, in the early stages, was consistently misrepresented.

Though it appeared that the treatment of the homopolar bond of the hydrogen molecule was an “extension” of the methods successfully used for the hydrogen molecule ion by Olaf Burrau (1927), there was a difference between the two cases that led to quite radical implications. It was the role of the Pauli principle. John Heilbron in his penetrating study of the origins of the exclusion principle talked about “one of the oddest of the instruments of microphysics” and that Wolfgang Pauli’s first enunciation in December 1924 had the form not of a dynamical principle but of the Ten Commandments (Margenau 1944; van der Waerden 1960; Heilbron 1983). During the ceremony at the Institute for Advanced Study at Princeton University to honor Pauli’s receipt of the Nobel Prize in Physics for 1945, Hermann Weyl talked of the Pauli principle as something that revealed a “general mysterious property of the electron” (Pauli 1946; Weyl 1946).

During the stay of Heitler and London in Zürich, Pauli’s paper on spin appeared.<sup>11</sup> Though they greatly appreciated it, they thought that it was not particularly satisfactory, because it was “a sort of hybrid between a wave equation and some matrix mechanics superposed on it. It was, so to speak, glued together, but not naturally combined together.”<sup>12</sup> In the case of the hydrogen molecule ion, its solution was a successful application of Schrödinger’s equation where the only forces determining the potential are electromagnetic. A similar approach to the problem of the hydrogen molecule leads to a mathematically well defined but physically meaningless solution—there can be no accounting of the attractive forces. There was, then, a need for an additional constraint, so that the solution would become physically meaningful. An interesting aspect of the theoretical significance of the original work of Heitler and London was that this additional constraint was not in the form of further assumptions about the forces involved. Invoking the exclusion principle as a further constraint led to a quite amazing metamorphosis of the physical content of the mathematical solutions. Under the new constraint, the terms formerly giving strongly repulsive forces gave strongly attractive forces. These terms became now physically meaningful, and their interpretation in terms of the Pauli principle led to a realization of the new possibilities provided by the electromagnetic interaction.

Later on, London proceeded to a formulation of the Pauli principle for cases with more than two electrons that was to become more convenient for his later work in group theory: The wave function can, at most, contain arguments symmetric in pairs; those electron pairs on which the wave function depends symmetrically have antiparallel spin. He considered spin to be the constitutive characteristic of quantum chemistry. And because two electrons with antiparallel spins are not identical, the Pauli principle did not apply to them, and one could, then, *legitimately*, choose the symmetric solution (Heitler and London 1927; London 1928).

With the Pauli principle, it became possible to comprehend “valence” saturation: It seemed reasonable to suppose that whenever two electrons of different atoms combine to form a symmetric Schrödinger vibration, a bond will result. As it will be repeatedly argued in the work of both Heitler and London, spin would become one of the most significant indicators of valence behavior and would forever be in the words of John Hasbrouck Van Vleck (a physicist from Harvard) “at the heart of chemistry” (Van Vleck 1970, 240).

### Reactions to the 1927 Paper

Right after its publication, it became quite obvious that the Heitler–London paper was opening a new era in the study of chemical problems. The fact that the application of quantum mechanics led to the conclusion that two hydrogen atoms form a molecule and that such was not the case with two helium atoms was particularly significant. Such a “distinction is characteristically chemical and its clarification marks the *genesis of the science of sub-atomic theoretical chemistry*” remarked Pauling (1928, 174), who later became one of the dominating figures in quantum chemistry. A similar view with a slightly different emphasis was put forward by Van Vleck (1928, 506): “Is it too optimistic to hazard the opinion that this is perhaps the *beginnings of a science of ‘mathematical chemistry’* in which chemical heats of reaction are calculated by quantum mechanics just as are the spectroscopic frequencies of the physicist?”

In their book on quantum mechanics for chemists, Pauling and E. Bright Wilson hailed the paper as the “greatest single contribution to the clarification of the chemists’ conception of valence” (Pauling and Wilson 1935, 340) that had been made since Lewis’s ingenious suggestion in 1916 of the electron pair (see chapter 2). Heisenberg in an address to the Chemical Section of the British Association for the Advancement of Science in 1931 considered the theory of valence of Heitler and London to “have the great advantage of leading exactly to the concept of valence which is used by the chemist” (Heisenberg 1932, 247). A. David Buckingham quoted William McCrea, who recalled his own attempts to solve the problem of the hydrogen molecule bond, when one day in 1927, McCrea told Ralph Howard Fowler that a paper by Heitler and London apparently solved the problem in terms of a new concept: a quantum mechanical exchange force. Fowler thought it was an interesting idea and asked McCrea to present the paper in the next colloquium—“which is how quantum chemistry came to Britain” (McCrea 1985; Buckingham 1987).

A meeting where questions related to chemical bonding and valence were exhaustively discussed was quite suggestive of the changes occurring among the chemists. This was the “Symposium on Atomic Structure and Valence” organized by the Division of Physical and Inorganic Chemistry of the American Chemical Society and held in 1928 at St. Louis. Chemists attending the meeting of the American Chemical Society

appeared to be sufficiently fluent in the ways of the new physics. George L. Clark's opening remarks are quite remarkable in that respect.

He talked of certain modes of behavior in a way ingrained among chemists and physicists. The former failed to test their well-founded conceptions with the facts of physical experimentation, and the latter did not delve critically into the facts of chemical combination. He criticized the firm entrenchment, as he called it, of chemists and physicists in their own domains, so that no comprehensive channels of communication between the two had been established nor had a language that would be accepted by both been developed. "The position of the Bohr conception has seemed so convincing that perhaps the majority of thinking chemists were coming to accept the dynamic atom, which is fully capable of visualization" (Clark 1928, 362).

Without denying one of the cardinal characteristics of the chemists' culture—that of visualizability—Clark was courageous enough to talk not of the majority of chemists but of the majority of *thinking* chemists. It was a small yet telling sign of the problems that were encountered at the beginning to convince the chemists about the importance and the legitimacy of using quantum mechanics.

Clark was not alone in attempting to specify the problematic relationship between the physicists and the chemists. Worth Rodebush, one of the first to receive a doctorate in 1917 from the newly established Department of Chemistry at the University of California at Berkeley under the chairmanship of Lewis, went a step further than Clark. The divergent paths of physicists and chemists had started being drawn together after the advent of quantum theory and especially after Bohr's original papers. But in this process "the physicist seems to have yielded more ground than the chemist. The physicist appears to have learned more from the chemist than the chemist from the physicist. The physicist now tells the chemist that his ways of looking at things are really quite right because the new theories of the atom justify that interpretation, but, of course, the chemist has known all the time that his theories had at least the justification of correspondence with a great number and variety of experimental facts" (Rodebush 1928, 511).<sup>13</sup> He gracefully remarked that it was to the credit of the physicist that he can now calculate the energy of formation of the hydrogen molecule by using the Schrödinger equation. But the difficulty in a theory of valence was not to account for the forces that bind the atoms into molecules. The outstanding task for such a theory was to predict the existence and absence of various compounds and the unitary nature of valence that can be expressed by a series of small whole numbers leading to the law of multiple proportions. The "brilliant theories" of Lewis accounted for the features of valence "in a remarkably satisfactory manner, at least from the chemist's point of view" (Rodebush 1928, 513). London's group theoretical treatment of valence—to which we refer in the next section—was considered as an important piece of work even though it did not answer all the queries of the chemist such as, for

example, the differences in degree of stability between chemical compounds. He was afraid that the rule of eight—the number of electrons in a closed shell—was being threatened, but there again it may be a kind of “chemical correspondence principle” because of the qualitative character of the chemical methods.

Van Vleck’s review of quantum mechanics presented at the symposium concentrated on explaining the principles and the internal logic of the new theory. He was quite sympathetic to matrix mechanics. He gave full credit to the work of Heitler and London, something found in most of Van Vleck’s papers through 1935, before he was convinced to use the more “practical” methods of Pauling and Mulliken (Van Vleck 1928). Van Vleck fully accepted Dirac’s attitude that the laws for the “whole of chemistry are thus completely known” and thought that the dynamics that was so successful in explaining atomic energy levels for the physicist should also be successful in calculating molecular energy levels for the chemist. The actual calculations may be formidable indeed, but the mathematical problem confronting the chemist was “to investigate whether there are stable solutions of the Schrödinger wave equation corresponding to the interaction between two (or more) atoms, using only the wave functions which have the type of symmetry compatible with Pauli’s exclusion principle.” Such a program for examining the implications of quantum mechanics for chemistry “has been made within the past few months in important papers by London and by Heitler. Although this work is very new, it is already yielding one of the best and most promising theories of valence” (Van Vleck 1928, 500). And he drew attention to the crucial feature of such an approach, lest the chemists “get the wrong idea.” The non-occurrence of certain compounds was not because the calculations yielded energetically unstable combinations, but because the corresponding solutions to the Schrödinger equation did not satisfy the symmetry requirements of the Pauli principle. The achievements of quantum mechanics in physics were summarized in ten points, and the section about chemistry was appropriately titled “What Quantum Mechanics Promises to do for the Chemist.” Great emphasis was placed on the importance of spin for chemistry, and it was shown that the Pauli exclusion principle could provide a remarkably coherent explanation of the periodic table. Its extreme importance was stressed elsewhere as well: “The Pauli exclusion principle is the cornerstone of the entire science of chemistry” (Van Vleck and Sherman 1935, 173). Nevertheless, if quantum mechanics was to be of any use in chemistry, one should go further than the periodic table and understand which atoms can combine and which cannot.

Among the reviews published at the time, Pauling’s article published in *Chemical Reviews* did much to propagandize quantum mechanics, explicitly aiming at the “education” of chemists in the ways of the new mechanics (Pauling 1928).<sup>14</sup> Pauling presented the details of the calculation by Burrau (1927) of the electron charge density distribution of the hydrogen molecule ion, because the original article was published in a journal “which is often not available.” Burrau was the first to integrate success-

fully the wave equation for the simplest molecule—the hydrogen molecule ion. He found a numerical expression for the electronic wave function in the field of the two nuclei; that is, he obtained the first numerical expression of a molecular (binuclear) orbital, together with values for the equilibrium internuclear distance, total energy, and vibrational energy of the lowest state.

The Heitler–London treatment of the structure of the hydrogen molecule was considered as “most satisfactory,” and it was repeatedly stated that in a few years, spin and resonance—which Pauling had, in the meantime, formulated, and which would eventually become his trademark—will provide a satisfactory explanation of chemical valence (Pauling 1928a, 1931, 1931a; Pauling and Sherman 1933, 1933a; Pauling and Wheland 1933) (see chapter 2).

Perhaps the most cogent manifestation of the characteristic approach of the American chemists was Harry Fry’s contribution in the symposium on Atomic Structure and Valence. He attempted to articulate what he called the pragmatic outlook. He started by posing a single question that should be dealt with by the (organic) chemists. What would be the kind of modifications to the structural formulas so as to conform to the current concepts of electronic valence? This, he insisted, should by no means lead to a confusion of the fundamental purpose of a structural formula, which was to present the number, the kind, and the arrangement of atoms in a molecule as well as to correlate the manifold chemical reactions displayed by the molecule.

It should here be noted that no theory in any science has been so marvelously fruitful as the structure theory of organic chemistry . . . When we are considering methods of modifying this structure theory of organic chemistry, by imposing upon its structural formulas an electronic valence symbolism, are we not, as practical chemists, obligated to see to it that such system be one that is calculated to elucidate our formulas rather than render them obscure through the application of metaphysically involved implications on atomic structure which are extraneous to the real chemical significance of the structural formulas, *per se* . . . The opinion is now growing that the structural formula of the organic chemist is not the canvas on which the cubist artist should impose his drawings which he alone can interpret . . . Many chemists believe that the employment of a simple plus and minus polar valence notation is all that is necessary, at the present stage of our knowledge, to effect the further elucidation of structural formulas. *On the grounds that practical results are the sole test of truth, such simple system of electronic valence notation may be termed ‘pragmatic.’* (Fry 1928, 558–559, emphasis ours)

“Chemical pragmatism” resisted the attempts to embody in the structural formulas what Fry considered to be metaphysical hypotheses: questions related to the constitution of the atom and the disposition of its valence electrons. It was the actual chemical behavior of molecules that was the primary concern of the pragmatic chemist, rather than the imposition of an electronic system of notation on these formulas that was further complicated by the metaphysical speculations involving the unsolved problems about the constitution of the atom. Fry had to admit the obvious fact that as

the chemists will know more about the constitution of the atom, they would be able to explain more fully chemical properties. He warned, though, that premises lying outside the territory of sensation experience are bound to lead to contradictory conclusions, quoting Immanuel Kant and, surely, becoming the only chemist to use Kant's ideas to convince other chemists about an issue in chemistry!

### Group Theory and Problems of Chemical Valence

The first indications that the work they started in their joint paper could be continued by using mathematical group theory involving molecular symmetry elements and operations are found in a letter from Heitler to London in late 1927.<sup>15</sup> By September, Heitler had gone to Göttingen as Born's assistant and London to Berlin as assistant to Schrödinger, who had succeeded Max Planck. Heitler was very excited about physics at Göttingen and especially about Born's course in quantum mechanics where everything was presented in the matrix formulation and then one derived "God knows how, Schrödinger's equation."<sup>16</sup> He believed that the only way the many-body problem could be dealt with was with group theory and outlined his program to London in two long letters.

His first aim was to clarify the meaning of the line chemists drew between two atoms. His basic assumption was that every bond line meant exchange of two electrons of opposite spin between two atoms. He examined the case with the nitrogen molecule and, in analogy with the hydrogen case, among all the possibilities, the term containing the outermost three electrons of each atom with spins in the same direction (i.e.,  $\uparrow\uparrow\uparrow$  and  $\downarrow\downarrow\downarrow$ ) was picked out as signifying attraction.

He became convinced that only by using group theory was it possible to proceed to a general proof. But if one assumed "that the two atomic systems  $\uparrow\uparrow\uparrow\uparrow$  . . . and  $\downarrow\downarrow\downarrow\downarrow$  . . . are always attracted in a homopolar manner. We can, then, eat Chemistry with a spoon."<sup>17</sup>

This overarching program to explain all of chemistry got Heitler into trouble more than once. Eugene Wigner used to tease Heitler, because Wigner was skeptical that the whole of chemistry had been explained. Wigner would ask Heitler: "[W]hat chemical compounds would you predict between nitrogen and hydrogen?" And of course, since he did not know any chemistry he couldn't tell me."<sup>18</sup> Heitler confessed as much in his interview: "The general program was to continue on the lines of the joint paper with London, and the problem was to understand chemistry. This is perhaps a bit too much to ask, but it was to understand what the chemists mean when they say an atom has a valence of two or three or four . . . Both London and I believed that all this must be now within the reach of quantum mechanics."<sup>19</sup>

Heitler, then, went on to work out in detail the methane molecule  $\text{CH}_4$ . C is in  $\uparrow\uparrow\uparrow\uparrow$ . (C has to be excited from its ground state in order to be  $\uparrow\uparrow\uparrow\uparrow$ . But this is consistent with experience.) There are exactly four different "hives" in the L-shell for four

electrons that are antisymmetrically combined. The four H atoms would be accordingly  $\downarrow\downarrow\downarrow\downarrow$ . Methane could be, therefore, reduced to the simple formula: The four atoms are attracted in a homopolar manner to the C atom, without, however, any repulsion among them. The tetrahedral arrangement resulted from this. The prospects from all these preliminary thoughts were quite promising “if it were possible to approximate better the whole damn thing.”<sup>20</sup>

London was in agreement with Heitler that group theory may provide many clues for the generalization of the results derived by perturbation methods. The aim was quite obvious: to prove that quantum mechanics stipulates that among all the possibilities resulting from the various combinations of spins between atoms, only one term provides the necessary attraction for molecule formation. Nevertheless, London was not carried away by the spell of the new techniques—as Heitler was in the company of Wigner and Hermann Weyl at Göttingen. London “did not join in my studies of group theory. He thought it was too complicated and wanted to get on in his own more intuitive way.”<sup>21</sup>

In Göttingen, Heitler started to study group theory intensively. Wigner’s papers had already appeared, and there was a realization that group theory could be used for classifying the energy values in a multibody problem as well as for calculating perturbation energies. The theory of the irreducible representations of the permutation group provided the possibility of dealing *mathematically* with the problems of chemical valence in view of the difficulties involved in dealing with the many-body problems. The unavailability of reliable methods for tackling many-body problems haunted London all his life, yet years later, this difficulty became peculiarly liberating for London, helping him to articulate the concepts related to macroscopic quantum phenomena such as superconductivity and superfluidity.

After moving to Göttingen, Heitler started publishing a series of papers dealing with the question of valence by using group theoretical methods. As described in a significant paper with Georg Rumer (Heitler and Rumer 1931), they were able to study the valence structures of polyatomic molecules and find the closest possible analogue in quantum mechanics to the chemical formula that represented the molecule by fixed bonds uniting two adjoining atoms. They found that the emerging quantum mechanical picture was more general and that the bonds were not strictly localized. Nevertheless, the dominant structure was, in general, the one corresponding with the chemical formula. But there were other structures that were also significant, and these structures were quite useful in understanding chemical reactions. He recollected that London “was the first [a long time before the Heitler–Rumer paper] who showed that the activation energies in the treatment of the three hydrogen atoms could be understood in quantum mechanics, and this method gave us then a general understanding for it.”<sup>22</sup> Later, Pauling called this a resonance between several structures. “A point which was violently objected to by the chemists was that both London and I stated that the

carbon atom with its 4 valences must be in an excited state . . . all this was later accepted by the chemists, but at that time I don't think the chemists did find this of much use for them."<sup>23</sup>

Convinced that it was impossible to continue his work in chemical valence by analytic methods, London also turned to group theory. By the middle of 1928, he drew a program to tackle "the most urgent and attractive problem of atomic theory: the mysterious order of clear lawfulness, which is the basis for the immense factual knowledge of chemistry and which has been expressed symbolically in the language of chemical formulas" (London 1928, 60). London's group theoretical approach to chemical valence was formed around three axes. First, anything that may give a rather strong correlation between qualitative assessments of a theoretical calculation and the "known chemical facts" provided a strong backing for the methodological correctness of the approach chosen by expressing the observed regularities as rules. Second, because analytic calculations were hopelessly complicated and in most cases impossible, the use of group theoretical methods was especially convenient when one was dealing with the valence numbers of polyelectronic atoms, as the outcome was expressed either as zero or in natural numbers. Third, the overall result was that the interpretation of the chemical facts was compatible with the conceptual framework of quantum mechanics. Using group theoretical calculations, one could hope "to discover in the quantum mechanical description conceptual facts which in chemistry have proven themselves in complicated cases as a guide through the diversity of possible combinations, and see them in their connection with the structure of atoms" (London 1928a, 459). Hence, he attempted to give the valence numbers of the homopolar combinations an appropriate interpretation that "rests on the conceptual representations" of wave mechanics. Within such a program, London intended to deal with the problem of the mutual force interactions between the atoms; to examine whether it was possible to decipher the meaning of the rules that the chemists had found in semiempirical ways and to place those on a "sound" theoretical basis; and to determine the limits of these rules and if possible to initiate a quantitative treatment of them.

But he was not at all certain that the principles considered so far in atomic theory could, in fact, be used for the realization of such a program. This was because the characteristic interaction of the chemical forces deviated completely from other familiar forces: These forces seemed to "awake" after a previous "activation," and they suddenly vanished after the "exhaustion" of the available "valences." By making use of elementary symmetry considerations, it was known that the mode of operation of the homopolar valence forces could be mapped onto the symmetry properties of the Schrödinger eigenfunction of the atoms of the periodic system and could be interpreted as quantum mechanical resonance effects. This interpretation was formally equivalent to its chemical model, that is, it produced the same valence numbers and

it satisfied the same formal combination rules, as they were expressed in the symbolic representation of the structural formulas of chemistry, that followed within the group theoretical possibilities as an immediate consequence of the Pauli principle in connection with the two valuedness of the electron spin. In particular, the fact that the valences were “saturated” proved in this context to be an expression of the restriction that the Pauli ban denotes for the occupation of equivalent states. Through group theory, London realized that the “uniqueness of the chemical symbolism is actually a consequence of the most fundamental theorems of the theory of the representations of the symmetric group” (London 1928b, 48).

London’s “spin theory of valence” dealt mainly with those cases where each electron in a pair comes from a different atom. He examined the conditions whereby electrons from different atoms can pair with each other so that the resultant spin of the pair was zero. An electron already paired with another electron in the same atom was not considered in this schema of pair formation for bonding. Two electrons in the same atom were said to be paired if they had opposite spins and all their other quantum numbers were the same. But such an electron that was already paired could become available for bond formation with an electron from another atom if it could be unpaired without the expenditure of too much energy. London claimed that an electron can be unpaired provided that the total quantum number  $n$  of that electron does not change. Such an unpairing was considered by London as an intermediate step in the formation of a compound (London 1928, 1928a, 1928b, 1929).

### **Erich Hückel: Nonvisualizability and the Quantum Theory of the Double Bond**

Heitler and London were led to tackle the problem of the chemical bond through their attempt to study the van der Waals forces. Their approach showed in no uncertain terms that the newly developed quantum mechanics would also be the appropriate framework for chemical problems. They attempted to bypass the calculational difficulties by using group theory and, most importantly, by *not* being faithful to one of the chemists’ cardinal “principles”—that of visualizability. Another parallel approach to chemical bonding was being developed in Germany. From the start it attempted to cater to the community of organic chemists despite its strong grounding in quantum mechanics.

For a long time, the work of Erich Hückel (1896–1980) and his role in establishing quantum chemistry has not been given the attention it deserves. This is no longer the case, and we owe it especially to the systematic and perceptive work of Andreas Karachalios (Parr 1977; Hartmann and Longuet-Higgins 1982; Brock 1992; Berson 1996, 1996a, 1999; Park 1999a; Kragh 2001; Karachalios 2003, 2010). Hückel’s contributions were mainly in the area of organic chemistry and more specifically on aromatic molecules and he had—through his talks and review papers—attempted to “talk”

especially to the organic chemists, trying to convince them of the possibilities arising from quantum mechanics.

Hückel's studies at the University of Göttingen were interrupted by the First World War, and he spent some time as an aid to Ludwig Prandtl, who was then involved in his ground-breaking studies in aerodynamics. Hückel completed his doctoral dissertation at Göttingen under Peter Debye in 1921, and he studied the properties of anisotropic fluids trying to detect the kind of structures occurring in liquid crystals using Debye's method of X-ray interference developed for the study of the atomic structure of crystals. No particularly pronounced space lattice structure was detected, but Hückel acquired significant experience in the use of physical methods for the study of chemical problems. His work on the bonding of the unsaturated and aromatic compounds followed the first papers he published together with Debye where they discussed issues in the theory of strong electrolytes.

For a year after receiving his doctorate, he was David Hilbert's assistant at Göttingen. At the time, Hilbert was lecturing on the special and general theories of relativity. The next offer was from Born, who had accepted a post at Göttingen, while the promised assistantship from Debye, who had in the meantime moved to Zürich, was being delayed in the cogwheels of the Swiss bureaucracy, which had very strict laws for the employment of foreigners. With Born he published a paper on the quantum theory of polyatomic molecules (Born and Hückel 1923), which involved rather complicated mathematical computations.

His participation in the "Bohr Festival" (Mehra and Rechenberg 1982, ch. 3) during summer 1922, where various issues in quantum theory had been intensely debated, underlined his conviction that the new theory had a lot to offer for chemistry. Starting in fall 1922, he officially became an assistant to Debye at the Eidgenössische Technische Hochschule Zürich (ETH). His main research topic was the theory of strong electrolytes, as experimental results, especially those concerning electrical conductance, yielded unexplainable deviations from the predictions of the theory. In their joint paper published in 1923, Debye and Hückel, using statistical thermodynamics, developed a new function for the ion distribution, and their theory gave satisfactory results for the freezing-point depressions and the limiting law of the electric conductance in dilute solutions.

Soon after receiving his appointment at Zürich, Hückel started working on his habilitation, which he completed at the end of 1924. In this work, he was able to extend the treatment of dilute solutions to solutions with high concentrations of electrolytes (Hückel 1925). This work in colloidal chemistry led to the writing of a book on adsorption and capillary condensation of gases and vapors on solid surfaces and porous bodies (Hückel 1928). The momentous developments of quantum mechanics took place while Hückel continued to be absorbed by his book, and it was due to Debye's pressure that he shifted his attention to the systematic involvement with

quantum mechanics. In 1928 in Leipzig, Debye had organized a meeting on “Quantum Theory and Chemistry.” The lectures were delivered by different people, including some of the protagonists in the developments of quantum mechanics, and Hückel attended the meeting. He spent 3 months in 1929 in Copenhagen, and it was finally Bohr who directed him to the study of double bonding.

Starting in fall 1929, he received a fellowship from the Emergency Association of German Science (*Notgemeinschaft der Deutschen Wissenschaft*). Through this fellowship, it became possible to work at the Department of Theoretical Physics of the University of Leipzig, where Heisenberg and Friedrich Hund were already professors of theoretical physics and mathematical physics, respectively. In fall 1930, Hückel was appointed a dozent for teaching “chemical physics” at the Polytechnic in Stuttgart in Ewald’s group where he stayed until 1937. In March 1934, he decided to join the National Socialist People’s Welfare organization (*Nationalsozialistische Volkswohlfahrt*, or NSV) (Karachalios 2003).

Hückel’s tenure at Stuttgart marked the beginning of a slightly different research program. He proceeded to study the binding state of alternating single and double bonds, something that, in effect, meant the study of the electron configuration of the carbon atoms in benzene and other aromatic compounds (Brush 1999). Mulliken later referred to the first of these papers (Hückel 1931) as “monumental” (Mulliken 1965, 8). This research was, in fact, his second habilitation (1931), as the one he had written on strong electrolytes was considered by the authorities as unsatisfactory because he was employed to teach chemical physics—considered part of physics and not of chemistry. The faculty regulations stipulated the submission of a separate thesis before he could make such a disciplinary transition from physical chemistry to chemical physics.

When Ewald emigrated, Hückel assumed teaching his lectures on theoretical physics between April 1 and September 30, 1937. In May 1937, Hückel became a member of the National Socialist German Workers’ Party (*Nationalsozialistische Deutsche Arbeiterpartei*, or NSDAP), and toward the end of year he was offered the position of extraordinary professor of theoretical physics at the University of Marburg—an offer that, despite the favorable assessments of his work by people like Sommerfeld and Heisenberg, may not have been independent of his joining the party. In fact, that was the reason Hückel gave, later on, for having joined the party.

### The Quantum Theory of Double Bonding

The concept of a double bond is as old as the proposal of the tetrahedral carbon atom—the bonding of two tetrahedrons connected along one edge. The experimentally observed rigidity of the double bonds could not be explained, and there was no quantum mechanical treatment for this kind of bonding. The problem had been discussed during the Leipzig meeting. Hückel had started to tackle this problem while in Copenhagen and continued to study it in Leipzig (Hückel 1930).

Hückel attempted to use classical interactions—such as dipole interaction—between the substituents to explain the observed rigidity against rotation, and he first tried to understand the stability of double bonding according to classical physics, but to no avail. He noticed, however, the unexpected way in which double bonds absorbed ultraviolet light and proposed that this anomaly may be due to the electronic structure of the double bond and, hence, the necessity for a quantum mechanical treatment of the phenomenon. He directed his efforts toward understanding the stabilization brought about due to the charge distribution of the electrons. Hückel moved along the following lines: He considered the oxygen molecule as a kind of “algorithmic device” and proceeded from  $\text{O}=\text{O}$  to formaldehyde ( $\text{O}=\text{CH}_2$ ) to ethylene ( $\text{CH}_2=\text{CH}_2$ ) by substituting the oxygen nucleus with a carbon nucleus with the removal of two hydrogen nuclei, and the resulting  $\text{CH}_2$  was then linked to oxygen. Through the same process, he “formed” ethylene.

Hückel started his treatment by choosing the electronic configuration of the ground state of the oxygen molecule proposed by John Edward Lennard-Jones (1929), even though he knew about the alternative suggestion by Hund and Mulliken:

$$(1s)^2 (1s)^2 (2s)^2 (2s)^2 (2p_+)^2 (2p_-)^2 (2p\sigma)^2 \{2p\pi_+, 2p\pi_-\}.$$

This arrangement implied that the oxygen molecule in its ground state involved a double bond with four valence electrons: two in the  $2p\sigma$  state and two in the  $\{2p\pi_+, 2p\pi_-\}$  state. The former gave rise to a homopolar valence bond (because of the antisymmetry of the electrons) and comprised one of the valence lines. Each one of the other two electrons occupied one of the two degenerate orbitals, hence the ground state of the oxygen molecule involved a triplet state, which is responsible for the experimentally observed paramagnetism of oxygen. Considering the ground state of formaldehyde ( $\text{O}=\text{CH}_2$ ) and by making a number of simplifying assumptions (such as, for example, neglecting the  $\sigma$ - $\pi$  coupling), he found that both the two  $\sigma$  as well as the two  $\pi$  electrons formed homopolar valence bonds. But the perturbation brought about by the two hydrogen substituents formed a splitting of the doubly degenerate  $\pi$  one-electron state into two different states. Then, there resulted two polyelectronic states. One is a singlet state and is diamagnetic (due to the orbital motion of electrons). The other is a triplet state and paramagnetic (due to electron spin and associated with unpaired electrons). It was not possible to calculate which state had a lower potential energy, and, hence, he could not reach a criterion for choosing the more stable configuration. He suggested that experimental results—not yet available—on the magnetic susceptibility of formaldehyde would be able to distinguish between the two. Nevertheless, through some analogical thinking he came to the conclusion that the  $\text{O}=\text{C}$  double bond was not the same as that of the oxygen molecule, and this was due to the hydrogen substituents. He continued in the same manner to “reach” ethylene. His overall conclusion for a quantum mechanical treatment of the double bond was

that it consisted of two different types of bonds, one  $\sigma$  bond and one  $\pi$  bond. The former had no stabilizing effect on the molecule's planar arrangement, whereas the latter was responsible for the fact that the substituents could not rotate freely around the double bond (Karachalios 2010).

Hückel could not be indifferent to the interpretative particularities of his theoretical treatment formulating, as it were, a serious epistemological challenge to the approaches of almost all the protagonists of quantum chemistry. He noted that his treatment of the double bond appeared to be coherent with Jacobus van't Hoff's overall approach for the rigidity of the double bond against rotation. But he was emphatic that his "theory does not completely conform with this picture because no *real meaning* is attached to the four valence directions depicted by van't Hoff; only the plane on which they lie in van't Hoff's picture has such a meaning" (Karachalios 2003, 77, emphasis ours).

The phrase "real meaning" refers to physical significance and, perhaps, physical reality—even though the notion of what is real, or of what has physical materiality, was not something quantum chemists dealt with in any systematic and philosophically strict manner. Yet, Hückel's theory shifted the emphasis on what was physically significant in van't Hoff's model from the four valences to the plane on which they lie, without, however, altering the model itself. As it often happened among quantum chemists, quantum mechanics reassessed one of the interpretative cornerstones of chemistry, that of visualizability. The latter, so closely attached to the classical worldview, could no longer take advantage of its heuristic role when quantum mechanics started to be widely used in the treatment of chemical problems. There have been many cases when quantum chemists would opt for the nonvisualizable representations in configuration space in order to stress that, perhaps, the strong affinity chemists had with visualizable entities and the tradition to present results in terms of visualizable entities may have become a rather serious hurdle in their attempt to adapt to quantum mechanics. But *at the same time*, pictorializing "entities" was not something to be dispensed with altogether because, especially in view of the impossibility to have analytical solutions, "pictorialization" had continued to be a particularly useful and, at times, effective way of dealing with chemical problems. This was not always so straightforward, and Hückel's interventions had underlined the difficulties involved: To talk of the changes brought about by the use of quantum mechanics in the stereochemical model—perhaps the "most visual" of all models—without disfiguring it altogether was a challenge in itself.

Comparing, in fact, Hückel's treatment of the double bond with that of Pauling and of John Clarke Slater, there appeared some nontrivial differences. As we show in the next chapter, Pauling's main theoretical entity for dealing with the two C=C bond was his directed  $sp^3$  hybrid orbitals. The overlapping of two such tetrahedrally directed orbitals gave the sought for stability of the double bond against rotation. The maximum

overlapping of the two eigenfunctions occurs when the two tetrahedral carbon atoms share an edge. Thus, Pauling's approach gave much credence to the original van't Hoff model, explaining at the same time the stability against rotation (Pauling 1931). Not much later, Mulliken developed a more satisfactory quantum theory of double bonding using group theory (Mulliken 1932c, 1932d, 1933).

Pauling and Slater justified the visual models of traditional chemists through skillful application of the mathematical language of quantum mechanics. Hückel's model, on the contrary, underpinned the organic chemist's classical visualizations while placing them at the same time on a new foundation that would ultimately articulate a new epistemological framework.

### Quantum Theory of Aromaticity

Hückel was able to provide a quantum mechanical explanation of why a number of properties of aromatic compounds were associated with a group of six electrons like in benzene—the “aromatic sextet” first noticed in 1925 by J. W. Armit and Robert Robinson, who had used Lewis's valence scheme (Armit and Robinson 1925). Hückel showed that these electrons, which formed a ring, formed in fact a complete closed shell, and he also explained a number of experimental observations on benzene (Hückel 1931, 213). Hückel's shift in emphasis was evident from his paper. He claimed that aromaticity was due to the number of electrons forming a complete electron shell, rather than the number of atoms forming a ring, thus providing an explanation of the stability of the aromatic cyclic systems.

Hückel improved his treatment of aromaticity in a second paper, through a method (referred to by Hückel himself as method II) that still bears his name: the HMO method (Hückel's molecular orbital method) (Hückel 1932; Pullman and Pullman 1952; Dewar 1969; Coulson, O'Leary, and Mallion 1978). The end result was a quantum mechanical treatment of aromaticity, through the  $4n+2$  (where  $n = 0, 1, 2, \dots$ ) rule as the criterion for aromaticity. The formula referred to the number of  $\pi$  electrons in a given organic cyclic compound, which would be classified as aromatic if the number was 2, 6, or 10. Furthermore, this explained the stability of the aromatic molecules with respect to reactions. One important result of his approach was that for aromatic and unsaturated compounds, the number of possible valence structures is not the same as the number of different states of determined energy, nor is a state of determined energy necessarily identified with a specific valence structure.<sup>24</sup>

Hückel's papers included rather involved mathematical calculations and did not make easy reading—especially for chemists, despite the fact that his work had been deemed as particularly significant for organic chemistry. The indifference of many chemists in Germany was not even shaken with Hund's 1933 survey article in the *Handbuch der Physik*. Hückel was indeed in a rather peculiar situation. His case was exceptional for while he worked in physical chemistry, he was able to overcome the

deficiencies of his training as an organic chemist by taking advantage of his brother Walter Hückel's expertise in the field, which probably helped him in asking the pertinent questions in organic chemistry to be answered in the framework of quantum mechanics.<sup>25</sup> But his successes were not appreciated either by physicists who did not care much about problems of organic chemistry or by organic chemists who were unfamiliar with the new techniques and their mathematical framework, despite a few who thought that such ignorance was not for the benefit of their craft.<sup>26</sup> By 1937, Hückel abandoned the field unable to challenge a scientific establishment in which German physicists and chemists were unwilling to accept research on the quantum mechanical properties of the chemical bond.

### **Hans Hellmann: Fundamental Theorems and Semiempirical Approaches**

Hans Hellmann (1903–1938) was born in Wilhelmshaven in Germany, and his father was a noncommissioned officer in the navy. He chose to leave Hitler's Germany because of his Jewish wife, settled in the Soviet Union, and was executed in the great purges. In 1922, he started attending classes at the Institute of Technology in Stuttgart planning to major in electrical engineering but soon changed to physics, and in 1925 at the University of Kiel he attended lectures by Kossel, who was among the first to discuss the electronic theory of the covalent bond. While at Kiel, he worked on experiments measuring the frequency-dependent dielectric constants of conducting hydrous salt solutions. He moved to Berlin where he worked with Otto Hahn and Lise Meitner on experiments synthesizing "radioactive preparations for physical research." In 1929 at the University of Stuttgart and working with Erich Regener, he received his doctorate with the thesis "On the Occurrence of Ions from the Decomposition of Ozone and the Ionization of the Stratosphere." This work showed that, contrary to the speculation that pairs of ions appeared when ozone was decomposed, what actually happened was the production of an extremely small number of such pairs (Schwarz et al. 1999, 1999a).

In the same year that Hellmann defended his dissertation, Erwin Fues was appointed to the chair of theoretical physics and applied mathematics at the Institute of Technology in Hannover and offered Hellmann an assistantship, which Hellmann accepted. In Hannover, Hellmann had the opportunity to discuss issues in various branches of chemistry, as there were many chemists in the Faculty of General Science. This turned out to be particularly useful for his future researches in quantum chemistry.

In 1931, he was appointed lecturer in physics at the Veterinary College at Hannover. In 1933, 1 month apart and independent of each other, Hellmann and Slater proved what came to be known as the molecular virial theorem—the possibility to calculate exactly the kinetic and potential energies for a stationary system if its total energy is

known. Hellmann showed that it was the relative reduction of destabilizing energy that contributed to the bond stability. He was, also, able to derive the variations of the energies as a function of the internuclear distance. In a way, Hellmann's work had a rather intriguing conceptual side to it: He attempted to *reformulate* the dominant view as to what caused the stability of bonds. It is interesting that the "physicist" Hellmann had adopted semiempirical methods in his theoretical calculations, where he made ample use of the experimentally known properties of the diatomic fragments occurring in a molecule.

Aware—as were most of the pioneers of quantum chemistry but not many of his German fellows—that results had to be made available to chemists in a special parlance, Hellmann together with W. Jost (a fellow assistant who was a physical chemist) published two papers discussing the "chemical forces" by using quantum mechanics (Hellmann and Jost 1934, Jost 1935). Later in the Soviet Union, he also wrote articles on quantum mechanics and chemical bonding, aiming primarily at chemistry-oriented audiences. He also delved into the intense debate around the issues of quantum measurement and, generally, of the possibilities offered by dialectical materialism for the further understanding of nature, without succumbing to the extreme ideological views of some of the popularizers of science in the Soviet Union.

Hellmann's leftist political views did not help him during the first months of Nazi rule in Germany. Things became even worse when in his application for the submission of the habilitation, as stipulated by the Reich Law of June 30, 1933, he had to include information about his wife being Jewish. He accepted the offer in 1934 of the post of "head of the theory group" at the prestigious Karpov Institute in the Soviet Union. The institute was in the Ukraine, which was also the place of his wife's origin. The institute had existed since 1918 and was dedicated to research in chemistry, and it had developed into a world class center with very important work in physical chemistry and quantum mechanics. By the time Hellmann arrived, there were already 150 scientists and 250 technical staff members working at the institute.

There he was associated with Ya. Syrkin, who later wrote one of the standard textbooks on quantum chemistry and who was to oppose his colleagues' critical stand against Pauling's ideas in quantum chemistry (see chapter 2). By the end of 1936, he had been granted a doctoral degree that made him eligible for a lectureship at universities in the Soviet Union. He was given various prizes for his research, was invited to present his research to the Academy of Sciences, and on January 1, 1937, he was promoted to a full member of the institute, a position that corresponded with a professorship.

The work he undertook at the Karpov Institute dealt with the investigation of the ways to derive the affinity relations between the various chemical elements. Hellmann put forth the notion that came to be known as pseudopotential. When atoms approach each other, valence electrons are coupled because of the Pauli principle. This creates

a repulsive effect between the occupied shells, because as a result of the Pauli principle, there is an increase in the electrons' kinetic energy. There is, thus, in Hellmann's words an "additional potential," later to be called pseudopotential: It is the potential that compensates for the electrostatic-nuclear attraction. Thus, the effective potential that now appears in the Schrödinger equation is the sum of the two. This expressed, again, his characteristic methodology: Hellmann proceeded to the determination of the value of this potential not only through approximate calculations when they were possible, but also through fitting to "experimental energies of suitable atomic states" (Schwarz et al. 1999, 16).

Despite his past as a lecturer in a chair of theoretical physics and applied mathematics, Hellmann was not among those who sought the strict application of formal mathematical methods while discussing issues in quantum chemistry. His was a semiempirical approach, followed by a careful analysis of some of the intricate problems in the development of quantum mechanics aiming basically at a chemistry-oriented audience. He was advocating the validity of physical laws for chemical phenomena, but at the same time he tried to avoid very strict and formal presentations. He made ample use of graphical methods, attempting, in a way, to circumvent the difficult problem of visualization in quantum mechanics generally, and quantum chemistry in particular. Hellmann the physicist, when it came to dealing with problems of (quantum) chemistry, was rather receptive to the possibilities offered through the semiempirical approach.

He claimed that "a purely theoretical derivation of properties of materials always means returning from quality to quantity," by which he meant that what one knows qualitatively can be physically explained if there is a (proper) theoretical derivation. The perception of quantum chemistry by chemists in the Soviet Union did not appear to have been any different from that of their colleagues in Germany. He wondered whether "organic and inorganic chemistry are engaged in organic and inorganic substances, which substances are the topic of theoretical chemistry? Purely theoretical substances? Does quantum theory have any useful role in chemistry at all?" (Schwarz et al. 1999, 15).

Hellmann believed that he had enough material to write a book. In fact, the manuscript in German was with Jost, who was seeking a publisher after Hellmann's forced emigration in 1933—to no avail, of course. The translated book was eventually published in the Soviet Union, appearing at the beginning of 1937 with the title *Quantum Chemistry*. An abridged German edition appeared the same year (Hellmann 1937). Hellmann had a tragic end. He became one of the countless victims of the purges of 1937. He was denounced by two colleagues (both having served as the Communist Party's local secretaries) at the Karpov Institute. He was arrested in March 1938 and executed on May 29, 1938. The only surviving document bearing his signature is his "confession," which "admits" deeds leading to espionage.

### Friedrich Hund: Foundations of Molecular Spectroscopy in Quantum Mechanics

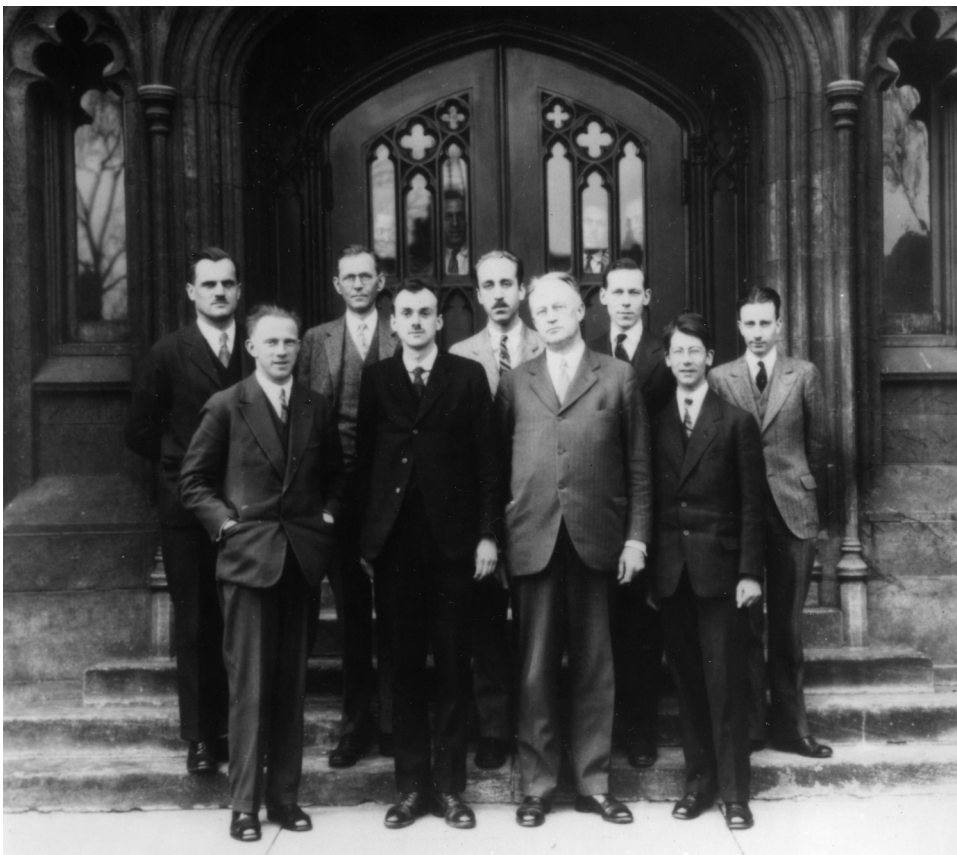
Among those who initiated research in quantum chemistry in Germany, Friedrich Hund followed a rather different path, inaugurating what came to be known as the molecular orbital approach. His contributions were remarkably close to Mulliken's, and both had a very cordial relationship. Born in Karlsruhe, Germany, Friedrich Hund (1896–1997) did not attend the Humanistische Gymnasium but instead the Oberrealschule and the Realgymnasium. He had a fair training in experimental physics but, since his high school days, he had shown a keen interest in mathematics, which he learned by himself, and thought for a long time of becoming a high school mathematics teacher. During the formative period before attending college, Hund equated physics with experimental physics and only later realized that the flourishing area of theoretical physics suited his interests better by fusing a solid mathematical methodology with a physical conceptual structure.

Hund attended the universities at Göttingen and Marburg and took courses in mathematics, physics, geology, and geography. In Göttingen, he took a course on quantum theory given by Debye and studied partial differential equations with Richard Courant. When Hund decided to become a theoretical physicist, he started to work with Born on the physics of crystals (*Gittertheorie*), as many of Born's students did, but he finally wrote his dissertation on the Ramsauer effect.

After completing his Ph.D. degree in Göttingen in 1922, he became Born's assistant and helped him write the book *Atommechanik* (Born 1960). Then he became privatdozent in the University of Göttingen in 1925, extraordinary professor in Rostock University in 1927, and professor at the same university 1 year later. From 1929 to 1946, he held a professorship of mathematical physics in Leipzig, after which he became successively a professor of theoretical physics in the universities of Jena, Frankfurt, and Göttingen.<sup>27</sup>

Hund's interest shifted to spectroscopy in the aftermath of Bohr's visit to Born's institute in June 1922 for "Bohr's festival," during which Bohr delivered a major series of lectures on quantum theory and atomic physics that were said to have "revolutionized" physics at Göttingen. He avidly discussed spectroscopy with James Franck, Hertha Sponer, Jordan, and Heisenberg (figure 1.2) and started to work on the interpretation of complex atomic spectra in terms of the Russell-Saunders vector model. The first to show how the notion of spin and the Pauli exclusion principle could be used to explain the periodic system of the elements, Hund's book *Linienpektren und Periodisches System der Elemente* contributed greatly to familiarize scientists with these two rules (Hund 1927).

In his last year as privatdozent at Göttingen, Hund divided his time between the study of complex atomic spectra and the spectra of molecules. The paper "Zur Deutung einiger Erscheinungen in den Molekelspektren" (Hund 1926) marked Hund's debut in



**Figure 1.2**

Group picture at the University of Chicago. Front row: Werner Heisenberg, Paul Dirac, Henry Gale, and Friedrich Hund. Back row: Arthur Compton, George S. Monk, Carl Eckart, Robert S. Mulliken, and Frank Hoyt.

Source: Max-Planck-Institute, courtesy AIP Emilio Segre Visual Archives. Gift of Max-Planck-Institute via David C. Cassidy.

the field of molecular spectroscopy. There, he discussed the nature of molecular electronic states from a theoretical point of view, introducing electron spin into band structure. He further suggested that in a diatomic molecule, the interaction of the two atoms produced a deformation of the spherical symmetry of the atomic field force into an axial symmetry around the internuclear axis, a perturbation that bore a strong analogy to the Stark effect. Based on this assumption, he suggested a molecular vector model and analyzed the different cases of band structure corresponding with different types of coupling between the electronic orbital angular momentum (specifically, its projection along the internuclear axis), the spin angular momentum, and the nuclear motion.

Later on, Hund used the new quantum mechanics to show that, in opposition to the old quantum theory, one could conceive an adiabatic transition from the states of two separated atoms to the states of a diatomic molecule, and then to the states of an atom obtained from the hypothetical union of the two atomic nuclei.<sup>28</sup> This fact allowed him to interpolate the electronic quantum states of a diatomic molecule between two limiting cases: the situation where the two atoms were separated (separated atom case) and the opposite situation where the two nuclei were thought to be united into one (united atom case). The idea was that one could imagine the molecule already latent in the separated atoms, so that the molecular quantum numbers existed already before the atoms come together, but started to play a dominant role (relative to the atomic quantum numbers) only in the situation where the two atoms were already at molecular distances from each other (Hund 1927a, 1927b).

Hund's contributions to elucidate the nature of the electronic states were almost "duplicated" by Mulliken, so that it becomes virtually impossible to analyze Hund's contributions to quantum chemistry without discussing simultaneously the approach of Mulliken. This we do analytically in chapter 2. As it often happened with approaches put forward initially by German and American scientists, they were frequently attempting to answer similar questions starting from different theoretical assumptions and developing complementary or even opposing methodologies. In chapter 2, we will discuss such issues when we deal with Heitler and London's later attempts to re-enter the field after the incursions of Pauling, Slater, and Van Vleck.

The case of the duo Hund-Mulliken is exceptional. After their first encounter and talks in 1927 when Mulliken visited Europe, the two became friends, discussing topics of common interest and complementing each other in their approaches to molecular spectroscopy and valence related questions. Their friendship, which grew stronger with time, seems to have facilitated their scientific dialogues and their symbiotic participation in building quantum chemistry.

Born in the same year, and revealing intertwined scientific trajectories up to 1937, Hund and Mulliken had very different backgrounds, yet very similar interests at the beginning of their careers, both being interested in band spectra.<sup>29</sup> In 1928, Hund had

completed a paper where he discussed various points concerning molecular orbitals. Just before sending his paper for publication, he was sent a preprint by Mulliken who had essentially done the same calculations. But Hund decided to go ahead and publish his paper because “Mulliken’s paper is rather American, e.g. he proceeds by groping in an uncertain manner, where one can say theoretically the cases for which a particular claim is valid.”<sup>30</sup>

### Some Further Remarks

Almost all the people involved in this first phase of the development of quantum chemistry—Heitler, London, Hund, Hückel, Hellmann—went through a university education where the mathematical training reigned supreme. Though nearly none was an expert in chemistry, almost all were highly sophisticated mathematically. Dirac’s claim may have gone unnoticed by the chemists and was thought of as something obvious by physicists, but what followed the Heitler–London paper was, in effect, an attempt at circumventing the catastrophic state of affairs prophesied by Dirac. A generation later, chemists would be in a position to articulate a set of sophisticated theoretical schemata with impressive empirical confirmations and claim that there was a new culture joined by all.

Nevertheless, historically the Heitler–London paper set the stage for the (uneasy) coexistence of chemists with quantum mechanics—definitely a physicists’ area of jurisdiction. For ages, mathematics and chemists did not make an agreeable contact. Hence, it was not all that welcome to have realized that one of the mysterious forces of chemistry—that of the homopolar bond—could be understood *only* in terms of quantum mechanics, bringing out at the same time the extreme significance of the exclusion principle. This principle acquired the status of a basic principle for chemistry. As Van Vleck and Sherman (1935, 173) aptly noted, “the Pauli exclusion principle is the cornerstone of the entire science of chemistry.” The Heitler–London paper made the community of physicists as well as chemists aware of the spectrum of possibilities of the newly formulated quantum mechanics. Though the possibilities covered a wide area, no one really knew how to realize them. The program was there, its promises loosely defined, but the attempts to get specific results were bogged down in almost insurmountable technical difficulties.

For a short period, group theory appeared to be doing the trick—a trick that could not be brought about by the use of the Schrödinger equation alone. Heitler and London demanded too much from the chemists: to accept the new mechanics and change their theoretical outlook. Using group theoretical calculations, one could hope to articulate new concepts, and London attempted to give the valence numbers of the homopolar combinations an appropriate interpretation that “rests on the conceptual representations” of wave mechanics. Furthermore, the use of group theory brought

about the realization that the “uniqueness of the chemical symbolism is actually a consequence of the most fundamental theorems of the theory of the representations of the symmetric group” (London 1928b, 48). But soon this approach was again at a dead end. And this dead end was of a technical as well as an epistemological character: Any theoretical attempt could not go any further than actually explaining what chemists already knew experimentally. There was no prediction. To use the theoretical apparatus of the physicists was one thing. To have theories with no predictive power was another, and particularly embarrassing, thing. The danger for the chemists was not to become physicists, but to become the physicists’ poor relatives, with theories that lacked one of the cardinal characteristics of the physicists’ theories—their predictive character. Examining the possibilities of group theory brought out the issue of theory *versus* rules. For a short period, it looked probable that group theory would lead to rules, something so dear to the chemists’ culture. And in this respect, one can sense questions related to contingency. The use of group theory delineated a totally different direction, where it all depended not on the empirically more satisfactory schemata of the rival approaches but on the consensus of the community as to what constitutes a more “proper/scientific/strict” theoretical schema.