Quantum Theory in Chemistry – Early Developments*

N. Trinajstić
The Rugjer Bošković Institute,
POB 180, HR-10002 Zagreb, Croatia

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The beginnings of quantum theory, and the main group of phycisists responsible for its early development, are briefly mentioned. The birthday of quantum chemistry is considered to be June 30, 1927 when the Editor (Karl Scheel) of *Zeitschrift für Physik* received the manuscript by Walter Heitler and Fritz London, who used the Schrödinger equation to study the electronic structure of a hydrogen molecule cation and a hydrogen molecule and introduced exhange forces between atoms as responsible for forming the chemical bond (there are also other views regarding the birthday of quantum chemistry). First quantum chemists, their contributions and first books on quantum chemistry are briefly mentioned. Early development of quantum chemistry is succinctly reviewed.

Key words: Quantum chemistry • quantum theory • molecular orbital (MO) theory • valence bond (VB) theory

Introduction

Quantum theory was born at the very end of the 19th century. *Max Planck* (1858–1947) delivered his historical lecture on December 14, 1900 at the meeting of the German Physical Society in Berlin. In this lecture Planck stated that paradoxes disturbing the classical theory of the emission and absorption of light by material bodies could be removed if one assumed that the radiant energy can exist only in the form of discrete energy packages. He called these packages light quanta. Thus, physics entered the 20th century with the new concept that the energy of a given physical system is quantized, that is, it cannot possess continuous but only discrete values.[1] Max Planck was awarded in 1918 the Nobel Prize in Physics for his concept of the quantum of energy.

The next thirty years witnessed a rapid development of quantum theory through the works of several young physicists who all got the Nobel Prize in Physics [*Max Born* (1882–1970), *Niels Bohr* (1885–1962), *Erwin Schrödinger* (1887–1961), *Louis Victor de Broglie* (1892–1987), *Wolfgang Pauli* (1900–1958), *Werner Heisenberg* (1901–1976), *Enrico Fermi* (1901–1954), *Paul Adrien Maurice Dirac* (1902–1984)].[2]

After this rapid development the pace slowed down and as of today the quantum theory is still not completed, especially in relation to the theory of relativity, the second great physics theory of the 20th century, introduced in 1905 (in its "special" form) by *Albert Einstein* (1879–1955).[3] However, in this essay we are interested in the early development of quantum chemistry, that is, the application of quantum theory in chemistry.

Quantum theory enters chemistry

In the third decade of the 20th century quantum theory entered chemistry for good. However, several problems of chemistry influenced the early development of quantum theory.[4] After Einstein in 1907 applied Planck's theory to the specific heats of solids,[5] *Walther Hermann Nernst* (1864–1941) and others came to believe that quantum ideas were essential for understanding the structure of matter. Besides the work on specific heats, quantum theory was also applied to molecular spectra. An important person in this regard was Danish physical chemist *Niels Bjerrum* (1879–1958), who successfully used quantum theory to make an interpretation of infrared spectra.[4] Thus, both the molecule and the atom pushed the development of quantum theory forward.

Schrödinger's wave equation represents a starting point for the entrance of quantum theory to chemistry. In 1924 *de Broglie* introduced the concept of the duality of matter, i. e., that all elementary particles, including electrons, possess both the corpuscular and wave-like character.[6] Three years later (1927), this proposal was experimentally con-

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firmed when two groups of experimental physicists (*C.J. Davisson* and *L.H. Germer* in the USA and *G.P. Thomson* in England; Davisson and Thomson received the Nobel Prize in Physics in 1937 for their work) showed that electrons could be diffracted by matter.

However, de Broglie was too slow to develop a mathematical theory of this concept. In 1926 *Schrödinger* published a general equation for de Broglie waves and showed its validity for all kinds of electron motion.[7] Remarkably, only a year after the Schrödinger equation was published, *Walter Heitler* (1904–1981) and *Fritz London* (1900–1954) produced the first quantum-mechanical treatment of a chemical system based on this equation.[8] At the time they were both at the University of Zürich and thus could discuss their work directly with Schrödinger who was also there. They acknowledged this in their paper.[8] On June 30, 1927 Heitler's and London's manuscript "Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik" was received by the editor (*Karl Scheel*) of *Zeitschrift für Physik.*[8] For many chemists this date is the birthdate of quantum chemistry.[9*] However, Heitler and London were never awarded the Nobel Prize for this achievement of utmost importance for chemistry.

Heitler and London considered two diatomic molecules made up from hydrogen atoms: (i) a hydrogen molecule cation H_2^+ consisting of two protons and one electron and (ii) a hydrogen molecule H_2 formed by two protons and two electrons. They approximately solved the Schrödinger equation for both cases and have shown that there exists an equilibrium structure of the lowest energy at certain distances between the two nuclei. The computed energy of these equilibrium structures was in fair agreement with the measured dissociation energies of H_2^+ and H_2 molecules. The important contribution of this work was the introduction of exchange forces between two atoms. These forces are responsible for the formation of covalent chemical bonds. Heitler-London's work really quantifies the intuitive, qualitative ideas of *Gilbert N. Lewis*[10] (1875–1946) (elaborated and popularized extensively by *Irving Langmuir* (1881–1957))[11] who described the covalent bond in terms of a pair of electrons shared by the pair of atoms they connect. Incidentally, in the paper by Heitler and London there is no reference to either papers by Lewis or Langmuir or to Lewis' 1923 book on molecular electronic structure.[12]

Evidently, they were not familiar (at least at first hand) with the work of Lewis and Langmuir on the nature of a chemical bond.

It is interesting to note the (optimistic and reductionistic) attitudes that the work by Heitler and London generated. For example, a year later (1928) *John Hasbrouck Van Vleck* (1899–1980; shared a Nobel Prize in Physics in 1977) wrote: "*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?*"[13] This is a human trait: At the beginning of anything we are always optimistic. Van Vleck's statement is nothing else but the echo of the statement made by *Louis Joseph Gay-Lussac* (1778–1850) in 1809: "*...we are not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation.*"[14] Because of this statement Gay-Lussac may be considered the forefather of theoretical (and computational) chemistry. However, computational chemistry finally received recognition through the 1999 Nobel Prize in Chemistry, half of which has been given to *John A. Pople*, the foremost computational chemist of our times.

Two years after Van Vleck's words (1929) Dirac stated: "*The underlying physical laws necessary for the mathematical theory of a larger part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble.*"[15] This led to statements such as "*Ever since the arrival of quantum mechanics in the 1920's it has been known that the chemistry is a* closed *science: in principle all chemical phenomena can be deduced from the laws of quantum physics*"[16], and a belief that everything in chemistry can be calculated. This kind of reductionism is the result of failing to see that there are "emergent" concepts in chemistry that even now have often not been unambiguously defined, though they are of great use for understanding chemical phenomena.[17] Besides detailed knowledge of the properties of one molecule it does not by itself give us any knowledge about the properties of other molecules. What is needed in chemistry, in addition to specific details about individual molecules, is an understan-

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*One of the three referees I had for this paper, argued as follows: "*Starting from the Abstract, the author repeatedly mentioned the 'birthday of quantum chemistry' in connection only with the Heitler-London paper of the H_2 molecule, 1927. However, this is only a birthday, if at all, of* molecular *quantum chemistry. MO theory was applied also to* solid states *at that early time by Felix Bloch who is also a Nobel Prize Laureate! He is regarded, in many books, as the ancestor of MO theory. Many scientists see the birthday of quantum chemistry in the publication of the Born-Oppenheimer (BO) approximation which is, in a special view, more fundamental than to calculate only a molecule, where the BO approximation was applied silently*". However, my standpoint is that Heitler and London have been first to study the nature of a *chemical* bond within the quantum theory. There is no need to remind the reader that the concepts of the chemical bond and the molecule are the *central* concepts in chemistry.

ding of property trends among and within broad classes of molecules. Therefore, everything cannot possibly be calculated in chemistry, there being so many possibilites.

Quantum chemistry

Chemical systems are many-body systems and thus too complicated to be solved exactly by the Schrödinger equation. Historically, two approximate approaches have been developed in chemistry to solve the Schrödinger equation. These are the valence-bond (VB) theory and the molecular orbital (MO) theory. Both of these approaches developed in parallel.

Heitler-London's paper[8] can be considered as the first paper of the VB theory.[18,19] Their method was extended and generalized by *Slater*[20] and *Pauling*.[21] Slater's and Pauling's works lead to concepts such as directed valence, hybridization, resonance theory, partial ionic character, electronegativity, and many other concepts which since have had numerous quantitative and qualitative applications. Thus, in the literature we sometimes find the term Heitler-London-Slater-Pauling (HLSP) or VB theory, e.g.[22]

The first MO papers may be considered works by *Burrau* on H_2^+ ion (which actually predates the work by Heitler and London by a few months; there is no given date when the manuscript reached the journal, but the printing of the journal was completed on March 19, 1927)[23] and *Condon* on H_2.[24] Starting from the Schrödinger equation for the H_2^+ ion, Burrau has shown that an electron is smeared out, in what is now called a molecular orbital, and thence provided a description of the one-electron bond. The early developers of the MO theory, curiously all born in the same year, were *Friedrich Hund* (1896–1997), *Erich Hückel* (1896–1980) and *Robert Saunderson Mulliken* (1896–1986).[25] Some early authors called the MO theory the Hund-Mulliken theory, since these two authors developed and extensively applied it, particularly to diatomic molecules, in a long series of papers.[26] Hückel developed a semiempirical π-electron MO theory, now known as the Hückel MO theory, using the set of approximations originally introduced by *Felix Bloch*[27] (1905–1983; who shared the 1952 Nobel Prize in Physics with *Edward Mills Purcell*), and applied it to benzene and benzenoid hydrocarbons. He also introduced a rule, now known as the Hückel $4n+2$ rule, to differentiate aromatic ($4n+2$) and non-aromatic ($4n$) systems (where n is a running index 1,2,...). In 1966 Mulliken was awarded the Nobel Prize in Chemistry, but Hund and Hückel were never recognized in this way.

The first book on quantum chemistry was written by *Hellmann*.[28] This book explicitly used the term *quantum chemistry*. An early influential book on quantum chemistry was by *Eyring, Walter* and *Kimball*[29] and is perhaps still the best introduction to quantum theory in chemistry. Hellmann's book is less known although it is also a very good source for entering quantum chemistry. Incidentally, the name of Hellmann is known to quantum chemists through the Hellmann-Feynman theorem.[28,30] This theorem is not useful for accurate calculations, but is very helpful in visualiazing energy changes. The interested reader may find the modern presentation of the Hellmann-Feyman theorem and its uses in references 31 and 32.

The most influential quantum-chemical book, spreading qualitative VB ideas, is certainly Pauling's *The Nature of Chemical Bond* which appeared in 1939.[33] This book has been reprinted many times in a few editions and is one of the most cited chemical books of all time.

Quantum chemistry before the Second World War was primarily in the hands of a few physicists and mathematicians. The use and potential of quantum chemistry was largely unknown to most chemists. There were many reasons for that. Traditionally experimental chemists did not want to bother with theories which could not help much in their immediate work. And in the USA this attitude was exacerbated by the influential editor (*Wilder B. Bancroft*) of the *Journal of Physical Chemistry*, with the dissenters from his traditionalist colloidal and thermochemical views, founding in 1933 the *Journal of Chemical Physics* (with Harold C. Urey as a managing editor). Most chemists found it overly difficult to follow the mathematics of quantum chemistry. And there was a tremendous computational problem involved; i. e., most of the interesting problems for chemists were out of reach of computational means that quantum chemists then had at hand. However, after the Second World War computers started to play a more important role and several books appeared which presented the frame and the predictive power of quantum chemistry in non-mathematical language. Perhaps the most influential postwar books on quantum chemistry were *Valence*[34] by *Charles Alfred Coulson* (1910–1974), whose first edition appeared in 1952, and *Molecular Orbital Theory for Organic Chemists* by *Andrew Streitwieser*, Jr.[22], whose first edition appeared in 1961. Coulson's book presented the elements of quantum chemistry and discussed both the VB and MO theories, while Streitwieser's book presented Hückel molecular orbital theory and its uses in organic chemistry with a brief reference to VB resonance theory only in the introduction. This is understandable since Streitwieser's book appeared when the dominance of the MO theory over the VB theory was presumed, because the MO theory was computationally much simpler in those days of limited computer power and because of many criticisms, most of which were in fact somewhat poorly justified.[35*] Today quantum-chemical computations and terminology are routinely used by chemists-at-large. Quantum chemistry became a standard tool of research in chemistry due to the availability of personal computers and easy-to-use software packages.

Concluding remark

The most important contribution of quantum theory, when applied to chemistry, is the development of the firm theoretical basis for the most important chemical theory, i. e., the structural theory of chemistry.[19]

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[*] One referee disagreed with this statement: "*This statement is entirely wrong. The opposite is true. To the end of the fifties, when computer facility came up, VB theory was recognized by quantum chemists being wrong way. At that time MO theory started its triumphal march. Streitwieser has precisely predicted this progress in his book. See also many other famous textbooks!*" However, there are a number of arguments contrary to this statement. This is supported by the recent revival of the VB theory in chemistry.[35]

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SAŽETAK

Kvantna teorija u kemiji – rani razvoj

N. Trinajstić

Ukratko je spomenut početak kvantne teorije i fizičari odgovorni za njen rani razvoj. Rođendanom kvantne kemije smatra se 30. lipnja 1927. godine, kada je urednik tada najuglednijeg časopisa za fiziku *Zeitschrift für Physik* Karl Scheel dobio rukopis *Waltera Heitlera* i *Fritza Londona* o razmatranju elektronske strukture molekule vodika i njenog kationa pomoću Schrödingerove jednadžbe. Postoje druga gledišta glede početka kvantne kemije. U ovom eseju prednost je dana radu Heitlera i Londona, jer su oni prvi razmatrali narav kemijske veze u okviru kvantne teorije. To je učinjeno zato jer autor smatra da su središnje koncepcije kemije narav kemijske veze i molekula.

Prikazan je ukratko rani razvoj kvantne kemije. Navedeni su prvi kvantni kemičari, njihovi doprinosi kemiji te prve knjige iz kvantne kemije.

Naglašeno je da je najvažniji doprinos kvantne kemije postavljanje strukturne teorije kemije na čvrsti teorijski temelj.

Institut "Rugjer Bošković",
P.P. 180, 10002 Zagreb, Hrvatska

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