REMEMBERING THE OLD TIMES OF THEORETICAL CHEMISTRY[*]

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1. Introduction

Can you imagine theoretical chemistry without computers? Well, this was the case until about 1948 or a little after. Yet, the origins of this discipline go back to earlier times. It is an offspring of the glorious epoch of theoretical physics which gave quantum mechanics to science and to the world. The bold idea of Louis de Broglie about the dual, wave-corpuscular nature of the electron and the subsequent epoch-making publications of Erwin von Schrödinger, Werner Heisenberg, and Paul Dirac made us understand the atom, crowning the pioneering works of Jean Perrin, Niels Bohr, and Ernest Rutherford.

But chemists are interested in molecules. The first quantum mechanical calculation on the hydrogen molecule was performed by Heitler and London in 1927 (Ref.[1]), only one year after Schrödinger's famous paper. This is usually considered as the year of birth of theoretical or quantum chemistry. It looked that quantum chemical calculations on larger molecules must wait until the arrival of computers.

They did not. What can be done without superior means of computation? A great deal can be done by the simple knowledge of the properties of atomic wave functions, the ways of putting them together to form molecular wave functions; in doing this, symmetry properties play a determining role. A master of this art was Robert Mulliken from the University of Chicago whom Coulson once called the doyen of theoretical chemists. Then came Linus Pauling's book[2] on resonance theory for which he received the Nobel Prize. More recently came the very successful method of Roald Hoffmann[3,4] (The Woodward-Hoffmann rules) who introduced the idea of orbital symmetry conservation combined with correlation diagrams. Yes, much can be done without detailed calculations.

Let us have a look at Herzberg's monumental trilogy[5–7]. The interpretation of molecular spectra is one of the most important aims of theoretical chemistry. Well, Herzberg was able to interpret an immense number of spectra of diatomic as well as small polyatomic molecules without hardly any reference to actual calculations. The correlation diagrams are the secret. The molecule is placed between the united atom and the separated atoms limit (or sometimes a united molecule) and then the interatomic distances are varied. Group theory is an indispensable tool. Without Wigner and Witmer's[8,9] work modern treatment of molecular structure and spectra would be unthinkable.

As to my personal experience, in 1947 I became member of a laboratory of quantum chemistry in Paris. In those years the best known groups of theoretical chemists were in Britain: the one of Coulson and the one of Lennard-Jones. Longuet-Higgins belonged to the former, Pople to the latter. Raymond Daudel introduced theoretical chemistry into France (and beyond). I left Hungary by the end of 1946 with a postdoctoral fellowship to work with Louis de Broglie; when he saw that I was more of a chemist than a physicist he sent me to Daudel who directed a group of about ten researchers under the nominal authority of de Broglie. Daudel has just founded the Centre de Chimie Théorique de France which later became the Centre de Méchanique Ondulatoire Appliquée of the CNRS. (Centre National de la Recherche Scientifique.)

2. The π-Electron Era

This was the π-electron era. In a first approximation π-electrons which form double and triple bonds in unsaturated organic molecules can be treated as a separate problem in the field of the σ-electrons considered as uniform. This focuses quantum chemical work on aromatic and other molecules containing conjugated double bonds (olefins, acetylenes). Benzene, higher aromatics and their substituted derivatives received much attention, not only from theoretical chemists but also from molecular spectroscopists. They absorb and emit light in the visible and near-ultraviolet region of the spectrum. So they were a relatively easy target for both quantum chemists and chemical spectroscopists. The methods of calculation applied to such molecules were approximate wave mechanical methods: the molecular orbital (MO), valence-bond (VB) and free electron (FE) methods. They all had considerable success with π-electron systems. The basic idea of the MO method goes back to the works of Hund and Mulliken in 1928. An early review was given by Mulliken[10]. The MO method had the brightest future, but in those times it was generally used in the simple Hückel approximation[11]. Even that was difficult

without computers. Just after the war, in 1947, we had only desk-calculators. The first hints about computers came in 1948. We were contacted by Bull and by IBM France. That was almost 50 years before Bill Gates.

In 1948 Daudel organized a memorable conference on quantum chemistry in Paris which many great men attended: Louis de Broglie, Max Born, Linus Pauling, C. Venkata Raman, Francis Perrin, R. S. Mulliken, C. A. Coulson, and others. This meeting contributed a great deal to establishig quantum chemistry as a recognized new discipline.

In subsequent years π-electron quantum chemistry flourished. Remarkable articles were published by Lennard-Jones[12]. Coulson and Longuet-Higgins[13,14], and others. Bernard Pullman who fought in the Free-French Army came home after the war and founded another theoretical chemistry laboratory in Paris with Alberte Pullman, Gaston Berthier, and others. Their book entitled *Les théories électroniques de la chimie organique*[15] published in 1952 is a sum of existing knowledge on conjugated organic molecules at that time. At a later stage Lionel Salem achieved an advanced wave mechanical, treatise on conjugated systems which still makes authority[16]. The book by Daudel, Lefebvre and Moser[17] published in 1959 had a different scope; it covered basic wave mechanical principles as well as methods and applications of quantum chemistry. An important contribution that originated in Daudel's laboratory was "la théorie des loges" (Odiot and Daudel[18–20]), an ingenious way of describing electronic distribution and localizability in molecules. It was followed by many attempts to investigate "atoms in molecules". At a later stage Daudel[21] gave a thorough discussion of the results obtained in this respect.

In spite of its rather approximate character the Hückel method rendered great services and was at the origin of a long and fruitful evolution. Per-Olov Löwdin reintroduced the long neglected overlap integrals. His ideas contained in an extensive paper in 1957 foreshadowed the forthcoming periods of quantum chemistry, in particular configuration[42].

The Hückel method implies some drastic approximations. The "linear combination of atomic orbitals" molecular orbitals (LCAO MO) are one-electron functions. The electrons are assigned to such molecular orbitals, two electrons at most being allowed to have the same MO, but one with spin projection α, the other with β, and the total wave function is taken as a simple product of the molecular orbitals of all the electrons considered.

This way of constructing the total wave function implies two fundamental weaknesses. (*1*) The Pauli exclusion principle is not adequately taken into account, since no spin wave functions are introduced. Therefore, spin is not allowed to exert any influence on the energy levels. An obvious consequence is the fact that excited states, where two electrons are in singly occupied orbitals, will have the same energy whether they are singlet or triplet. (*2*) Since every electron has an MO which is computed as if other electrons were not present, this method actually neglects the mutual repulsion between electrons.

Some of the shortcomings of the simple LCAO MO method can be compensated for by determining certain quantities such as the Coulombic and resonance integrals (α and β or γ with the notation of those times) empirically by comparison with experimental data, rather than computing them theoretically. This renders the method semi-theoretical, not a glorious

procedure. Yet under the given circumstances in the late nineteen-forties and early nineteen-fifties this had to be done and it helped molecular science progress. Even much later theoretical methods applied to larger molecules contained some occult empirical elements.

The important next step was to include spin explicitly making the total spin-orbital wave function of any stationary state antisymmetric with respect to the exchange of the coordinates of any two electrons in order to satisfy the Pauli principle. If we neglect magnetic interactions, energies of members of the *same* multiplet will be the same since the total wave function will be simply a product of an orbital function and a spin function. At least spin is allowed in this way to influence the electronic energy levels, and make the difference between singlets and triplets, in particular. The wave functions are introduced in the form of Slater determinants which give automatically antisymmetrized wave functions in their study of the electronic spectrum of benzene. Ethylene was first treated by Hartmann[23] and an improved treatment was given by Parr and Crawford[24] in their seminal paper of 1948. This treatment entails many integrals: molecular integrals which are subsequently expressed in terms of atomic integrals. For this the LCAO MO were used. Computing these integrals was not an easy task. Parr and Crawford had the merit of correcting some of the errors made by previous authors. So quantum chemistry departed on a correct footing.

At my beginnings I had problems even with the simple Hückel method. I went through the literature hoping to find a detailed example of such a calculation. At long last I found a not-so-well known paper by Coulson which appeared in the Transactions of the Faraday Society. There he gave some details. Much later, in 1964, I published a book on "Electronic Spectra and Quantum Chemistry"[25]. Remembering the difficulties of my young age I gave detailed examples of calculations using the simple Hückel LCAO MO method, the antisymmetrized MO method, configuration interaction, self-consistent field MO, … Did this help anybody? I can only hope.

I am reproducing from that book a list of the early collections of atomic integrals. Lest we forget. Some people worked hard fifty years ago. Even then some approximations had to be made, especially for three- and four- centre integrals. Some of us still remember Mulliken's approximation. (Replacing $\psi_a\psi_b$ by $1/2\ S_{ab}[\psi_a^2 + \psi_b^2]$ where S_{ab} is the overlap integral.)

Kotani, Amemiya, Ishiguro, Kimura: *Table of Molecular Integrals* (Tokyo: Maruzen, 1955).

Preuss: *Integraltafeln zur Quantenchemie*, 4 vols. (Berlin: Springer-Verlag, 1956, 1957, 1960, 1961).

Roothaan: *Two-center Coulomb Integrals between 1s, 2s, and 2p Orbitals* (Special Technical Report) (The University of Chicago, 1955).

Miller, Gerhauser, Matsen: *Quantum Chemistry Integrals and Tables* (Austin: University of Texas Press, 1958).

Sahni, Cooley: *Derivation and Tabulation of Molecular Integrals*, (Technical Note D146-I) (Washington, D.C.: National Aeronautics and Space Administration, 1959).

More data can be found in the following publications:

Kotani, Amemiya, Simose: Proc. Phys. Math. Soc. Japan *20*, extra number 1(1938); *22,* extra number 1 (1940).

Kopineck: Z. Naturforsch. A *5*, 420 (1950); A *6*, 177 (1951); A *7*, 785 (1952).

Barnett, Coulson: Philos. Trans. R. Soc. London A *243*, 221 (1951).

Roothaan: J. Chem. Phys. *19*, 1445 (1951).

Ruedenberg: J. Chem. Phys. *19*, 1459 (1951).

Ruedenberg, Roothaan, Jaunzemis: J. Chem. Phys. *24*, 210 (1956).

Roothaan: J. Chem. Phys. *24*, 947 (1956).

Preuss: Z. Naturforsch. A *8*, 270 (1953); A *9*, 375 (1954).

Boys, Cook, Reeves, Shavitt: Nature *178*, 1207 (1956).

Mulliken, Rieke, Orloff, Orloff: J. Chem. Phys. *17*, 1248 (1949) (overlap integrals).

Coulson: Proc. Cambridge Philos. Soc. *38*, 210 (1941).

Parr, Crawford: J. Chem. Phys. *16*, 1049 (1948).

Brennan, Mulligan: J. Chem. Phys. *20*, 1635 (1952).

Scrocco, Salvetti: La Ricerca Scientifica *21*, 1629 (1951); *22*, 1766 (1952); *23*, 98 (1953).

Murai, Araki: Prog. Theor. Phys. *8*, 615 (1952) (heteronuclear).

This list is far from complete.

A decisive step forward was made by Boys who first used Gaussians to compute atomic and molecular integrals[26–28]. This made calculations much easier.

The next step was to introduce configuration interaction. In 1949 Coulson and Fischer[29] suggested that what we formerly called states should be called configurations and the word "state" should be reserved for energy levels obtained as a result of a configuration – interaction calculation. If we had the exact wave function a configuration would be a good representation for a given state. Since, however, our functions are approximate, obtained through a variational treatment the configurations can actually mix under appropriate spin and symmetry conditions, the state functions will be linear combinations of wave functions of the configurations. In the case of ethylene for example, limiting the problem to the two π-electrons, there are three configurations:

The first and third can mix. If on the other hand we consider C=N instead of C=C, all three configurations can mix. In one of my early unknown papers I could show that they mix quite appreciably[30]. For the polyelectronic case the number of mixing configurations becomes tremendous, so configuration interaction calculations are a major problem of quantum chemistry. Singly excited, doubly excited, how far to go with energy differences, etc. takes a great deal of experience and judgement. This is well beyond the scope of this paper which intends merely to remember old times.

However, it would be hard not to mention the very successful multi-reference-double-excitation-configuration method (MRD-CI) due to Buenker and Peyerimhoff[115] and the alternant molecular orbital method of Pauncz[112].

The other "great leap forward" was making the wave functions self-consistent.

In most molecular problems in wave mechanics the approximation is made that each electron can be regarded as being in a stationary state in the field of the nuclei and the other electrons. As a consequence the molecular wave function is expressed as a product of one-electron wave functions or spin orbitals.

We quote from D. R. Hartree[32], *Calculation of Atomic Structures* [p. l8]: "For such an approximate wave function ψ, $|\phi_1(j)|^2$ gives the average charge density resulting from the presence of electron j in wave function ϕ_1, and this suggests that each one of these functions ϕ_1, ϕ_2, … ϕ_n should be determined as a solution of Schrödinger's equation for one electron in the field of the nucleus and of the total average charge distribution of the electrons in the other wave functions. In such a treatment, the field of the average electron distribution derived from the wave functions ϕ_1, ϕ_2, … ϕ_n must be the same as the field used in evaluating these wave functions. This aspect has led to the term 'self-consistent field' for the atomic field so determined".

This idea implies the iterative nature of the method. For if we want to determine the field acting on a given electron we have to know the wave functions of all the others. However, we do not know more about them than about the chosen one. Now we quote from Coulson[31].

"Suppose that there are n electrons in our atom. Then let us first guess plausible wave functions for each of these electrons. …Now choose one of the electrons and find the average field provided by all the others. … This process allows us to write down, and then to solve, the wave equation for our chosen electron. We obtain what may be called a first-improved wave function for this electron. This new function may next be used to calculate the average field for a second electron, and enables us to get a first-improved wave function for this electron also. The process is continued until we have a complete bunch of first-improved orbitals. In the same way starting with these we may improve them, one by one, and calculate second-order a.o.'s. This technique is continued until successive iteration makes no appreciable difference to the orbitals. We may then say that the set of a.o.'s are self-consistent."

Fock[33] adapted the method to the very important case where the wave functions are given in the form of Slater determinants. Roothaan[34] has shown that the Hartree-Fock method can be applied with a molecular orbital taken as linear combinations of atomic orbitals. He first worked out the LCAOSCF theory for closed-shell ground states. The calculation of the energies of excited states is more complicated. In most cases excited configurations contain simply filled orbitals and their wave function contains more than one Slater determinant. The conditions of self-consistency for such wave functions were given in different manners by Lefebvre[35], McWeeny[36], and Roothaan[37].

Configuration interaction and self-consistent field remained until this day the most advanced methods of quantum chemistry and they are not mutually exclusive. A variety of methods were proposed to make such calculations easier and, of course, a great deal became possible by using advanced computer techniques.

In the meantime two approximate methods were proposed by Pariser and Parr[38] and by Pople[39] which were widely used. At that point the transition from empirical to nonempirical methods was, to some extent, disappointing. In particular, the electronic excitation energies obtained were rather far from reality. One may say in a not very scientific manner, that in removing about half of the approximations involved with the

empirical methods we diminished the chance for the various errors to cancel each other. Therefore Moffitt[40] and Pariser and Parr[38] proposed to compromise by reintroducing a reasonable amount of empiricism into the nonempirical methods. This was done by neglecting differential overlap and computing certain integrals empirically. Using the Wannier-Löwdin[41] orthogonal atomic orbitals gave a certain amount of justification to these approximations. This method was applied with great success to aromatic and heteroaromatic molecules. Pople[43] reviewed these applications up to 1957. In a series of works Dewar[44], Pople[45], Murrell[46], Longuet-Higgins[47], and McEwen[48,49] reexamined the spectra of aromatic hydrocarbons and their derivatives, combining the LCAO SCF method with perturbation calculations. They also studied some of the ions and free radicals of these molecules. Brion, Lefebvre and Moser[50] proposed other ways of obtaining SCF wave functions.

An interesting point is that the similarity of this method to the simple Hückel method makes it possible to justify the basic approximations of the latter in the case of conjugated hydrocarbons. This was surprising and encouraging at the same time. The simple LCAO and valence-bond methods are sometimes called "naive" methods. As Daudel put it "The naive methods are less naive than they seem to be"[51].

This is about where we stood at the end of the nineteen-fifties. Much of theoretical chemistry was still a π-electron molecular orbital theoretical chemistry.

However, chemistry is not only ground-state chemistry. The electronic spectra of aromatic and other conjugated organic molecules were, from the beginning, a prime target for quantum chemical calculations. These semi-empirical calculations were quite successful and by the mid-nineteen-fifties the spectroscopy of such molecules was well understood.

In addition to molecular orbital methods free electron methods were also instrumental in this. One can think of the works of Platt[52,53], Kasha[54] or H. Kuhn[55] in this respect.

Before closing my reminiscences on the π-electron era I have to say a word about the valence-bond method. There was a time when it gave as much hope for the treatment of larger molecules as did the molecular orbital method. It was actually initiated by Heitler and London who were the first to treat the problem of the hydrogen molecule by a quantum mechanical method. Also, it is behind Pauling's resonance theory[2] which in those times was widely used by chemists. In the valence-bond method the molecular wave function is built from atomic orbitals just as in the molecular orbital method, but with the important difference that the total wave function belonging to the various energy levels of the molecule is constructed directly as a product of atomic orbitals without forming LCAO molecular orbitals. Spin is included right from the beginning and the spin functions are chosen so as to make the total wave function anti-symmetric with respect the exchange of the coordinates of two electrons. As a consequence of the Pauli principle, if there is a bond between two atoms, the two atomic orbitals forming the bond must overlap and therefore the two electrons must have opposite spin projections. This allows a variety of coupling schemes, called "structures". They were called effective if the "bond" is between two neighbours and ineffective otherwise. In the case of benzene, for example, these so-called canonical structures are the two Kekulé-type and three Dewar-type structures. The total wave function is then constructed as a linear combination of wave functions

which the molecule would possess if it could be represented by the respective structures alone. This procedure appears to conform more to chemical intuition than the molecular orbital method. I myself liked it very much in my youth and wrote a substantial chapter on it in my book which appeared in 1964 (Ref.[25]). Hartmann[56] and Seel[57] found ways of treating triplet states by the valence-bond method. As to polar "structures" Sklar[58] in his early paper (1937) on benzene made an attempt to include them and in 1950 Craig[59] published a series of papers on butadiene and benzene showing how this can be done.

In more recent times attempts were made to revive this method. Unfortunately, its relative complexity seems to preclude the possibility of competing successfully with the molecular orbital method. The book by Epiotis[60] is well worth reading, however.

Free-electron methods were also historically important for the treatment of the electronic spectra of π-electron systems. In these methods the wave functions of the electrons in a conjugated system are those of particles moving freely along the bonds. This idea was introduced by Pauling[61], Lonsdale[62] and Schmidt[63]; subsequently it was developed into a comprehensive system for the treatment of conjugated molecules by Platt[52,53] (rotator model) and H. Kuhn[55] (metallic or electron gas model). The free electron methods contributed a great deal to the general understanding of the electronic spectra of aromatic molecules, in particular that of Platt whose classification of states and notations are still sometimes used. Many years ago, I reviewed free electron methods in my above mentioned book[25].

Substituted derivatives of aromatic molecules also received a great deal of attention. The elegant experiments of Förster[66] (1950) showed that in OH and NH_2 substituted aromatic compounds the acidity and basicity of the molecule changes with the state of electronic excitation. In two of my unknown papers[67,68] I could show that this parallels large changes in electron density distribution. This is known to have important photochemical consequences. All over these years the Czech school pioneered the structure and reactions of heteroatomic systems. (See, for example, R. Zahradník[64], R. Zahradník, J. Koutecký[65].)

This section on π-electrons may seem to be too long. But theoretical chemistry matured on them.

3. The σ-Electron Era

Predictably, the π-electron era had to come to an end. Attempts to include the σ-electrons and the single bonds were made using bond or group orbitals. However, this is not really satisfactory, especially not when electronic excited states are involved. I felt very strongly about it. So one day in 1953 I called on Professor Daudel who was the chief of the laboratory to which I belonged at that time and asked him for permission to do some work on saturated hydrocarbons. As a result we published a preliminary note in 1954 (Ref. [69]) and later in 1955 already at Université de Montréal I published a long paper in the Canadian Journal of Chemistry[70]. These were to the best of my knowledge the first applications of the Hückel molecular orbital method to σ-electron problems and saturated organic molecules. I proposed three different approxi-

mations. The simplest of these was the "C" approximation. I am citing from the book on "Semiempirical wave mechanical calculations on polyatomic molecules", which we later published with Professor Daudel[21].

"The idea underlying this method is that, as Hückel was able to extract the π-electrons from conjugated molecules and treat them as a separate problem, it may be possible to separate the C–C bonds from the C–H bonds in saturated molecules and still be able to account for some characteristic properties of these molecules. There is clearly much less hope for such an approximation to be successful than there was for the Hückel method. While π-orbitals have a nodal plane where σ-electrons have their greatest density, no such difference exists between orbitals in C–C and in C–H bonds. Yet, one may hope that, in a rough approximation, the C–H bonds, in which the electrons are more tightly bound than in the C–C bonds make a constant contribution to the total energy in different paraffin molecules and to the electronic charge distribution in the C–C bonds.

Thus in the original "C" approximation, all H orbitals and all carbon sp^3 hybrids linked to the H orbitals were disregarded. For the remaining sp^3 orbitals, all the Hückel Coulomb integrals α_C were made equal, as were all the resonance integrals $\beta_{C–C}$ between atoms which are "chemically" bonded together. Non-neighbour interactions and all overlap integrals were neglected."

For the resonance integral between two sp^3 hybrids on the same carbon atom, a parameter (*m*) was needed. To obtain information as to its value, this latter parameter was varied. Subsequently Yoshizumi determined its value empirically[71].

Fukui, Kato, and Yonezawa[72,73] applied this simple approximation with surprising success to the calcutation of bond dissociation energies, total energies, and ionization potentials of normal and branched paraffins and many of their substituted derivatives. Taking the energy of the highest occupied orbital for the ionization potential (Koopmans' theorem[74]), they found an almost perfect parallel with experimental values. This led them to the well known frontier orbital considerations which turned out to be important for the following of chemical reactions. Both Fukui[72,73] et al. and Klopman[75] obtained encouraging results in their studies of saturated molecules using this simple "C" approximation.

A step forward was the "H" approximation[70]. In the "H" approximation all sp^3 hybrids and all hydrogen ls orbitals were included separately for the first time in a semiempirical treatment. Overlap integrals were fully taken into account in this approximation. They have, of course, high values for *s*-orbitals. The parametrization of this method is somewhat delicate. I proposed a set of parameters in my original paper; later Fukui et al.[73] used a somewhat different set. They obtained fair agreement with observed ionization potentials and heats of formation and used the electronic charge densities in the highest occupied molecular orbital as a reactivity index and found good correlations with the speed of metathetical reactions.

Fukui has reviewed in two publications[76,77] applications of the "H" approximation to problems of chemical reactivity. I should like to mention an earlier (1958) and often overlooked work by Del Re[78,79]. He put the differences in α proportional to differences in electronegativity, and in addition took into account the effect of all adjacent atoms on a given α. This leads

to a set of interdependent auxiliary Coulomb parameters, and the whole procedure approaches the electronegativity equalization requirement which is at present often applied. He computed electronic charge densities for many compounds and obtained dipole moments and quadrupole coupling constants in fair agreement with experimental values.

The next stage was the extended Hückel method.

Many years earlier Mulliken[80] and Wolfsberg and Helmholtz[81] suggested a very simple type of parametrization for Hückel calculations which greatly facilitates their extension to σ-electron problems. The Coulomb integrals for an orbital i ($\alpha_i = H_{ij}$) are taken as the appropriate valence-state ionization potentials and the resonance integrals ($\beta_{ij} = H_{ij}$) are expressed as

$$H_{ij} = 0.5\, K\, (H_{ii} + H_{jj})\, S_{ij}$$

All that is needed for this are overlap integrals, which can always be calculated and valence-shell ionization potentials.

Hoffmann[82,83] took up this parametrization and with a very rapid computer program he was able to apply it to a wealth of molecules with all valence electrons taken into account. Instead of using hybrid orbitals, as had previous authors, he used pure atomic orbitals and included all interactions and all overtop integrals. This is a crude method but it has extreme versatility. It can be applied without difficulty to three-dimensional molecules with the possibility of varying the assumed geometry. It soon revealed itself as an effective method of exploring equilibrium geometries, potential surfaces, energy differences between conformers, and other properties of three-dimensional molecules.

Pople and Santry[84] in 1963 presented a critical Hückel study related to saturated molecules. In particular, they studied the causes of delocalization of σ-electrons. They were able to show that, although the delocalization correction to the energy is appreciable, this is consistent with the approximate additivity of bond energies. (In the ground state.)

The logical next step in the study of σ-electron systems was to adapt the Pariser-Parr-Pople method for the treatment of such systems. A number of attempts have been made to apply semiempirical methods to saturated molecules. I would like to mention the one of Brown and Heffernan[85]. They pointed out in 1958 that when the electronic charge density changes on an atom the core Coulomb integral is not the only one to charge. The change has an influence on the orbital exponent itself and therefore all selected integrals must change. This idea was the basis of their variable electronegativity SCF (VESCF) method.

Then came the CNDO method due to Pople, Santry, and Segal[86,87]. It became the most widely used of the semiempirical methods applicable to all-electron problems and is amenable to a variety of adaptations and improvements. Pople et al. originally proposed two different approximations: "complete neglect of differential overlap" (CNDO) and "neglect of diatomic differential overlap" (NDDO).

In the CNDO method first the usual PPP approximations are made; that is, both overlap integrals and differential overlap are neglected. It is most important to note that some of these will concern differential overlap between atomic orbitals on the *same* atom.

At this stage Pople et al. observed that the "theory is not invariant under a rotation of local axes or under hybridization".

Furthermore, since sets of hybrid and the related "pure" atomic wavefunctions are connected by an orthogonal transformation, the results should be unchanged by such a transformation. However, the neglect of differential overlap in integrals taken over pure orbitals would not, in general, make vanish an integral taken over hybrid orbitals based on the former.

Invariance is restored in both cases if the following new approximation is adopted: "The electron interaction integrals $\gamma_{\mu\nu}$, are assumed to depend only on the atoms to which the atomic orbitals χ_μ and χ_ν belong and not on the actual type of orbital". This is the most characteristic approximation of the CNDO method.

I am not trying to go any further. We are well in the nineteen-sixties and at the "end of the beginning" of theoretical chemistry. The *ab initio* era was on and highly performing computers made quantum chemistry a computational science. The very efficient programs of Pople's group played a decisive role in this.

The semiempirical epoch was reviewed by Pople and Beveridge in their "Approximate Molecular Orbital Theory"[87]. It contains a thorough treatment of CNDO methods and their applications. Daudel and Sándorfy[21] attempted to cover the field up to 1970.

Sinanoglu and Wiberg[88] organized a memorable conference on "Sigma Molecular Orbital Theory" at Yale University. This conference and the book which was subsequently published in 1970 by Yale University Press marked, in my opinion, the watershed between old and new times, between semiempirical and *ab initio* quantum chemistry. In the words of Sinanoglu and Wiberg "Quantum chemistry may be considered to be entering a new phase." …"Semiempirical methods allow calculations on a large number of molecules at little cost. They have been useful as guides in chemical applications, and have gained more and more importance in both organic and inorganic chemistry. However, these methods often involve drastic and as-yet untested approximations. They need, therefore, to be used judiciously." … "Clearly, for predictions on chemical reactions, σ-electrons are essential".

Then came *ab initio*, density functionals, high level configuration interaction and computers and computers. I remember a conversation with Mulliken many years ago. He used the expression "Computer Calculations" with a slight contempt. The implication was that it is just technology, the principles count. Yes, but there are technological advances that transform life and science. One may think about printing, photography, the steam engine, electricity, aeroplanes, semiconductors, nuclear energy, lasers, television, and computers. At present quite advanced calculations can be made not only on electronic energies and charge distribution, but also on even more delicate problems involving molecular vibrations and rotation, even quadrupoles and nuclear spin.

The widely used programs due to Pople's group are playing an essential role.

However, it would be unjust not to add the following.

Historical attempts were made to obtain truly accurate results on small systems at an early stage. Hylleraas[89,91] with his correlated wave functions obtained a near-perfect solution of the problem of the helium atom. Subsequently these were taken up again by Roothaan and Weiss[90]. Another great success of early quantum mechanics was the treatment of the hydrogen molecule by James and Coolidge[92,93]. Like Hylleraas they introduced the interelectronic separation into the variation function. They also carried out similarly successful calculations on some of the excited states of the H_2 molecule. Kołos and Roothaan[94] in 1959 made a two-pronged attack on the ground state and lower excited states of the hydrogen molecule. They first used the best Hylleraas type correlated function, then a James and Coolidge type function with up to 50 terms. For the internuclear distance they obtained 0.74127 Å, the experimental value being 0.74116 Å. A great, hard won Victory.

4. Valence and Rydberg Excited States

I should be tempted to stop at this point. Two important comments have to be made, however. Chemistry is not only ground-state chemistry and chemical bonds are not the only ones that keep molecules together. There are excited states at the one end and weak interactions, van der Waals forces and hydrogen bonds at the other.

Let us first remember the excited states as they were dealt with in quantum chemistry. Molecular spectroscopy is an old science, theoretical chemistry was no prerequisite for it. At least not molecular quantum chemistry. With a basic knowledge of atomic structure and well founded procedures using group theory, correlation diagrams, the Mulliken-Walsh[95] rules, a glorious field has been developed. Think about the lifetime work of Mulliken, the books of F. Hund[96], Eyring, Walter and Kimball[97], H. E. White[98], G. W. King[99], and above all, the monumental volumes of Herzberg[5–7,100]. They contain solid knowledge on small molecules and molecular species, ions and free radicals including those is space. In a recent book B. Stoicheff[101] presented the scientific and human biography of Herzberg which reflects a whole epoch. Quantum chemistry comes into the picture when larger molecules are examined. I have mentioned the great success of quantum chemistry relating to aromatic and other conjugated organic molecules. This was achieved by semiempirical molecular orbital methods with a non-negligible contribution by valence-bond and free-electron considerations. Spectra are characterized by frequencies, intensities and band width; theoretical chemistry can assess all three.

Saturated paraffinic hydrocarbons absorb only in the far ultraviolet where the bands to higher electronic levels of π-electron systems are also found. The spectroscopy of larger organic molecules is sometimes called chemical spectroscopy. The word "chemical" indicates a practical aspect and there is nothing vigorous about it. There are no physical or chemical spectra, only spectra. Often the information obtainable from rotational and even vibrational fine structure has to be sacrificed, but on the other hand chemical knowledge and comparisons between parent molecules are of help with the interpretation of the spectra.

Curiously, the electronic absorption spectra of saturated hydrocarbons were not known until 1967, except the one of methane. That year they were published by Lombos, Sauvageau, and Sándorfy[102] and by Raymonda and Simpson[103] but while Simpson's group interpreted them in terms of a bond orbital method, we assessed them in Rydberg terms. This goes back to a suggestion made by Mulliken in 1935 (Ref.[104]). That in atomic spectra there are Rydberg series is known to any

student. For a long time it was not widely known that molecules also have Rydberg states. Niels Bohr seems to have been the first to have drawn attention to this. The physicists concentrated on diatomic molecules. As to larger, basic organic molecules, Price and his coworkers[105] pioneered the field from the experimental side and Mulliken[106,107] from the theoretical side. Let us cite Herzberg[7]: "More and more highly excited states are obtained by bringing an electron from one of the orbitals filled in the ground state to higher and higher orbitals. These higher orbitals are more and more like atomic orbitals and therefore give rise to Rydberg series of electronic states whose limit corresponds to the complete removal of the electron considered, i.e. to an ionization limit of the molecule". The lower Rydberg states can mix with valence states of the same symmetry and this is photochemically very important. The Rydberg excited states are today a prime target for high resolution molecular spectroscopy ("ZEKE"[108–110] spectroscopy), photoelectron spectroscopy and photochemistry. As to larger molecules Robin summed up the field in three volumes[111]. Rydberg states add a new dimension to theoretical chemistry. The bulk of the merit in this respect belongs to Buenker and Peyerimhoff. Their most important papers started appearing in 1970, but this field is somewhat beyond the scope of these reminiscences. Yet, I would like to refer to an early review by Peyerimhoff[113] and to their chapters written for our book on "The Role of Rydberg States in Spectroscopy and Photochemistry"[114]. Those of Grein and Hachey and Lefebvre-Brion should also be cited in this context. These advanced treatments use *ab initio* methods with a very great number of judiciously chosen configurations. The Rydberg orbitals are strategically located on given bonds or groups.

The electronic transitions best known to chemists are valence (or intravalency) transitions because the wave functions of both the ground and excited states are built exclusively from atomically unexcited atomic orbitals. The visible and near-ultraviolet spectra of aromatic and conjugated olefinic hydrocarbons and their heteroatomic derivatives have been interpreted quite satisfactorily within this framework. The following question, however, is quite legitimate: why do we build our molecular orbitals only from atomically unexcited atomic orbitals? This is only justified by the fact that they suffice to give a fair description of ground states and the lower valence excited states. When we go higher, Rydberg states become a fact of life. Computational techniques for entering Rydberg orbitals into the LCAO scheme consist in building them from atomic orbitals corresponding to higher principal quantum numbers. Such techniques were elaborated and perfected by Buenker and Peyerimhoff[115–116]. I am now citing from Peric and Peyerimhoff[114].

"At first sight any classification of molecular excited states in terms of atomic states as defined by principal, angular and magnetic quantum numbers is surprising. The lower symmetry of the external potential in molecules compared to atoms would speak against such characterization. However, from the earliest quantitative theoretical investigations on low-lying excited states in small molecules such states, which show close resemblance to atomic (united atom or Rydberg) states, are well known. Their occurrence can be explained by the fact that an electron far away from the nuclei experiences a nearly spherical (point charge) potential from the remaining cation.

This simple consideration, however, shows clearly that the distinction between valence (similar electronic spatial extension as the ground state) and Rydberg states (much larger electronic spatial extension than the ground state) breaks down if the molecules becomes larger. From several studies carried out in the past it became obvious, that in systems with more than 5–10 non-hydrogen atoms mixed valence-Rydberg states are frequent".

Then from Buenker, Hirsch, and Yan Li[114]:

"When configuration interaction (CI) calculations became feasible at the *ab initio* level toward the end of the 1960s, there was a widespread tendency to overlook the importance of Rydberg electronic states in molecular spectra. The semiempirical calculations which were available before this time rarely if ever treated other than valence states, as, for example, in the Hückel and Pariser-Parr-Pople treatments of π-electron systems. Rydberg states were well-known from atomic spectroscopy, and as early as 1935 Price[105] had been able to assign them in molecular spectra. The attitude nevertheless persisted among most theoreticians active in electronic structure calculations that states with such diffuse charge distributions were of secondary interest at best because they were not expected to interact strongly with conventional valence states and transitions to them were thought to be comparatively weak. To this can be added the fact that it has always been relatively difficult to achieve a satisfactory description of Rydberg states by semiempirical methods, so there was no effective way to test the above hypotheses prior to the advent of *ab initio* treatments".

Rydberg theoretical chemistry and spectroscopy of typical organic molecules, ions, and radicals was the main subject of some conferences. The first one, "Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet". (Valmorin, Québec 1973; organized by Sándorfy, Ausloos, and Robin) brought together spectroscopists, photochemists and theoretical chemists; A. E. Douglas, W. C. Price, Th. Förster, M. B. Robin, S. P. McGlynn, P. Ausloos, D. W. Turner, H. Hartmann, S. D. Peyerimhoff, and others were there, a rare assembly of experts in different but related fields[118].

Rydberg quantum chemistry is a relatively new sector of quantum chemistry and the subject matter is far from being exhausted.

Another domain in which theoretical chemistry played a prominent role is that of charge-transfer complexes. There too, while the original impetus did not come from calculations, computerized quantum chemistry is taking over as a means of treating such systems. Charge-transfer spectra were known in the nineteen-twenties[119–120]. In those times most cases of charge transfer complexes were inorganic, but the field spread over to organic chemistry soon after. According to Mulliken's theory[123,124], the ground state wave function of donor-acceptor complexes is essentially a no-bond wave function, while the wave function of the excited state describes a polar bound state. The transition is then from a no-bond ground state to a charge transfer excited state. (This is the opposite of the case of alkali halides.)

The field of charge-transfer spectra is a very well reviewed field. An excellent review relating mainly to inorganic compounds was given in 1942 by Rabinowitch[125]. Later Andrews[126], Orgel[127], McGlynn[128], and Murrell[129] offered general reviews which treat the problems relating to molecular complexes from a variety of points of view. The "bible" of the field is Mulliken and Person's "Molecular Complexes[130].

The spectra of transition metal complexes distinguish themselves by rather conspicuous features. They have absorption bands in the visible due to their low-lying excited states. The central ions all possess incomplete $3d$ or $4f$ shells. These spectra became understandable in 1951 when Ilse and Hartmann[131] had the idea of applying crystal field theory to these complexes. The degeneracy of the five $3d$ subshells is lifted under the octahedral, tetrahedral, etc. symmetry of the field of the ligands, and transitions are possible between the resulting states. It is sometimes said that this is obvious. It was certainly not in those times. This is a tremendous field; many books and reviews appeared on it. It is beyond the scope of these reminiscences, however.

5.　Weak Intermolecular Interactions

Chemistry is not only the domain of chemical, covalent, or electrovalent bonds. Weak ligands, due to van der Waals interactions, and hydrogen bonds are also very important. It is also a field where the junction with thermodynamics is the most readily made.

The concept of hydrogen bonding was introduced around 1920 by Latimer and Rodebusch[132]. Hydrogen bonds are just as ubiquitous in our world as chemical bonds. This applies to both the organic and mineral worlds. Life could not exist without them. I think it is fair to say that hydrogen bond studies became a field of science with the Symposium on Hydrogen Bonding held at Ljubljana in 1957, organized by Professor D. Hadzi[133]. Among the theoretically inclined contributors one can mention Linus Pauling, J. A. Pople, N. Sheppard, G. C. Pimentel, S. Bratos, E. Lippert, R. Blinc, C. A. Coulson, E. R. Lippincott, L. Hofacker, N. D. Sokolov, M. Davies, M. Eigen, A. Terenin, and others.

Many of the "secrets" of hydrogen bonding are linked to the great breadth of the infrared stretching bands of OH (or NH, etc.) bonds. Bratos and Hadzi in 1957 (Ref.[134]) presented a complete theory introducing vibrational anharmonicity as the decisive factor. This was the subject of animated discussions at the second hydrogen bond conference which took place at Schloss Elmau in Germany, organized by E. Lippert. A long series of meetings followed, until this day. The field of hydrogen bonding is still very much alive. Advanced theoretical works are due to Witkowski and Maréchal[135], Sokolov and Savelev[136], Lippincott and Schröder[137] and many other authors. I would like to mention our volumes on hydrogen bonding published in 1976 (Ref.[138]).

It was logical that theoretical chemistry penetrates into the bio-medical field. A. and B. Pullman were the major artisans of this field. Their extensive *Quantum Biochemistry*, was published in 1963 (Ref.[139]). This too became an immense field.

As to *Weak Intermolecular Interactions in Chemistry and Biology*, the "Bible" is the book by Pavel Hobza and Rudolf Zahradník[140] first published in 1980. It is not up to me to review that very important field.

I have to emphasize that I did not attempt to write the history of theoretical chemistry or of a part of it. These reminiscences go to about 1960 only, although some references to more recent works were inevitable. Some of the famous theoretical chemists are mentioned in the text, others whose impact was felt mainly after 1960 could not or hardly be mentioned: Buckingham, Čížek, Clementi, Csizmadia, Dalgarno, Davidson, Jortner, Karplus, Koutecký, Kutzelnigg, Lefebvre, McWeeny, Mezey, Michl, Morokuma, Paldus, Pauncz, Pulay, Ruedenberg and many others, not to speak about the younger generation.

Gerhard Herzberg, Robert Mulliken, Roald Hoffmann, Kenichi Fukui, John Pople, Walter Kohn, were awarded the Nobel Prize. The time will come when somebody will write the history of quantum chemistry which has become a tremendous field. Good luck!

In 1967 R. Daudel (France) with P.-O. Löwdin (Sweden), R. G. Parr (U.S.A.), J. A. Pople (U.K. and U.S.A.), and B. Pullman (France) founded the International Academy of Quantum Molecular Science based at Menton (France). It lends additional prestige to the community of theoretical chemists.

These reminiscences are the result of a conversation I had with Professor Zahradník at the Czech Academy of Sciences for which I am very indebted. Unfortunately, I could not possibly make a good job. First of all, I am too old (82). Then I was not active at every phase of the evolution of theoretical chemistry. I left quantum chemistry for molecular spectroscopy at an early stage. So my report is biased and both too short and too long.

At our epoch everything tends to be too long. Daily newspapers behave like magazines, magazines like books and books are 800 pages long. This is why we have to cut our forests which make oxygen for us. Daily newspapers often contain 60 to 100 pages of which perhaps 6 to 10 are readable. The contents of 800 page books could often be compressed to 80, sometimes 8. Even my report is too long.

It is also too short, because I am not able to make all the important points; nor can I render justice to all the protagonists. Many hundreds more references should be cited. My ways of putting things reflect only my personal views.

I consider myself as a man of the street in theoretical chemistry. But well, in a democracy men of the street are entitled to their opinions. There is a kind of democracy underlying science. Normally, in a scientific publication the author should not show his face. Well, I have shown a part of mine. I probably forgot many things that should have been said. When you are 82, dear Reader you will understand.

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C. Sándorfy (*Département de chimie, Université de Montréal, Montréal, Québec, Canada):* **Remembering the Old Times of Theoretical Chemistry**

After recalling the early stages of quantum chemistry, a more detailed and systematic description of the post-war period (approx. 1945–1960) follows. The essential features of both π-electron and σ-electron eras are described: the simplest versions as well as procedures including electron repulsion are considered. Then attention is paid to valence and Rydberg excited states. The review is closed by remarks on hydrogen bonds and other weak intermolecular interactions.