

Several Stories from Theoretical Chemistry with Some Russian Flavor and Implications for Theorems of Chemistry, Vagueness of its Concepts, Fuzziness of its Definitions, Iconicity of its Language, and Peculiarities of its Nomenclature

Andrei L. Tchougréeff^[a,b]

We present an informal discussion of the problems related to emergence and development of theoretical chemistry concepts and their relation to those of quantum mechanics and general mathematical thinking. This also brings us to a discussion of axiomatization of chemical knowledge, relation between iconic language of (organic) chemistry and symbolic language of physics, relations between molecular orbital and

valence bond pictures of molecular electronic structure and other similar problems. Because of the thematic orientation of the present issue of the *Int. J. Quantum Chem.* Russian contributions to setting and solving the above problems are highlighted. © 2015 Wiley Periodicals, Inc.

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Introduction

This article arose from two author's talks given, respectively, at the Workshop on valence bond (VB) theory (July, 17–23, 2012,—Université Pierre et Marie Curie, Paris)^[1] and the 14th V.A. Fock Meeting on quantum and computational chemistry held in Samara (Russia; August, 18–22, 2014), and from some seminar talks largely intended to explain to physicists a chemical point of view upon electronic structure of molecules and solids. Also an announcement of the plans for a special issue of *HYLE—International Journal for Philosophy of Chemistry*—devoted to interrelations between chemistry and mathematics (two issues of great interest appeared meanwhile)^[2] forwarded to me by an old friend of mine, Richard Dronskowski, some years ago and an invitation from another good friend of mine, Andreas Savin, to take part in a collective paper of a new format,^[3] which I could not make real, turned on reflections on topics more general than everyday scientific interests.

Preparing this text, I realized that the title of the entire special issue is not original. “Theoretical Chemistry in Russia” was the title of a paper^[4] devoted to an episode evolving in the Soviet Union in 1949–1951, which completely confused Western observers. That story was rather sad and made one of the Western colleagues to ask the personage of Figure 1* during a

Meeting on quantum chemistry held in the Soviet Union about 1963 something like: “what is actually the Russian contribution to quantum chemistry?” The reply was the name of the personage of Figure 2 after which the conversation had switched to a different topic.[†] All this crystallized (not fully) in the following “several stories with Russian flavor,” representing some ideas related to mathematics and chemistry, symbolic and pictorial languages of physics and chemistry, respectively, to chemical bonding and its relevant measures, new semiempirism in quantum chemistry as a way out of some of its old problems, to fuzziness of chemical concepts and even to chemical nomenclature.

Chemistry and Mathematics

Chemists love mathematics,[‡] but most of them have problems to congest the standard calculus course. Chemists also love topology^[3] although not many of them can precisely explain what a hell it is, that is to say—*platonically*. The reason is twofold. First is the immense efficiency of the “topological”

*As you may be aware, the *Int. J. Quantum Chem.* has recently undergone a relaunch by the efforts of its Managing Editor Dr. M. Cavalleri, who meanwhile proposed me to prepare the present thematic issue. Now it represents much more modern publication media. Among its new features is that the review papers are accompanied by the authors' portraits. The present author considers it as natural to accompany the discussion of very humanitarian questions by the portraits of important, but sometimes forgotten or unexpected, contributors. In the Chemistry Department where the present author had a honor to graduate, at certain point, everyone who wanted (and had to: it was mandatory—no nonsense with “courses by student's choice”) pass an exam in “History of Chemistry” had to be sure that (s)he is able to name five famous chemists of the past by photos arbitrarily torn from a deck of ca. 100 of them. The nation has to know its heroes.

[a] A. L. Tchougréeff
Moscow Center for Continuous Mathematical Education, 119002 Moscow
Russia.
E-mail: tch@elch.chem.msu.ru

[b] A. L. Tchougréeff
Moscow State (Lomonosov) University, Moscow, 119992, Russia
Contract grant sponsor: RFBR; contract grant number: 14-03-00867.

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[†]Prof. N.D. Sokolov told this story to the present author about the year 2000 during a discussion of the destiny of the Fock Meetings launched in 1998 and happily survived until now. (Available at: <http://www.qcc.ru/~fock/meeting.en.php>).

[‡]I.A. Misurkin. A remark made to the present author when caught by him—author's PhD advisor—at a long derivation of something which now cannot be remembered any more.

Andrei L. Tchougréeff is a Principal Scientist at the Lomonosov Moscow State University (MSU) and the RWTH Aachen University. He studied Chemistry at the MSU (MSc, 1982). His PhD (1989, Karpov Institute) dealt with theory of conducting polymers. After postdoctoral period spent in the USA, France, and Germany (1991–1995) he rejoined the Karpov Institute where habilitated in 2004. Since the year 1998 he organizes prestigious V.A. Fock Meetings on Quantum and Computational Chemistry. His research is focused on the electronic structure of complex systems. He (co)authors over 100 research articles (see <http://www.qcc.ru/~tch/publist.html>) summarized in the Monograph "Hybrid Methods of Molecular Modeling".



language of organic chemistry. It is the chemists' mother language. Second, it is the disaster that happened to the mathematical education of chemists like all students of natural Sciences.^[5] It is difficult to be inspired by a "Math" course whose summit is the least squares method. Poor knowledge of mathematics dramatically affects an ability to consume quantum mechanics. Dealing with students of quantum chemistry not "having taken" quantum mechanics is our everyday life now. In subsequent sections we discuss the quantum mechanical/chemical reasons of efficiency of the "old" language of organic chemistry in a historical perspective and try to pave the way towards more general synthesis of the quantum chemical and topological ideas.

Ab initio

The origins of the unease between chemistry and mathematics have to be ascribed, probably, to the personage of Figure 3 who expressed serious doubts with regards to prospects of chemistry to become an area of application of mathematics and thus a *proper* science.^[6] Although a student of himself disprove this conclusion of the famous teacher soon after it had

been presented to the public,^[7] we dare recollect the personage of Figure 4 who pretty much *before* the concerns had been formulated insisted (Item 26)^[8] on the mathematical perspective of chemistry. The quotation is pretty eloquent:

Quantam lucem spagiricae scientiae Mathematicae accendere valeat, ille, qui hujus sacris initiatus est et jam quaedam scientiae naturalis capita, ut est Hydraulica, Aërometria. Optica etc., feliciter mathematice pertractata novit, praevidet. Etenim omnia ea, quae alias in incerta, clara, certa et evidenter reddidit. Et licet plerique Chymiam mechanices principiis stabiliri atque in scientiarum numerum referri posse eant inficias, ... Verum enimvero, si illi, qui omnes dies suos fumis et fuligine offuscarunt, quorumque cerebrum, chaos quoddam ac indigesta experimentorum moles obruit, sanctissimis Geometrarum legibus, quas olim Euclides severe observaverat, ... instrui non essent pertesi, intimius certe naturae adyta, ... possent penetrare. Profecto cum Mathematici per combinationem paucarum linearum quam plurimas veritates eruunt, cur et non Chymici ex tanta experimentorum farragine plura deducere possint, nullam rationem praeter Matheseos ignorantiam video.

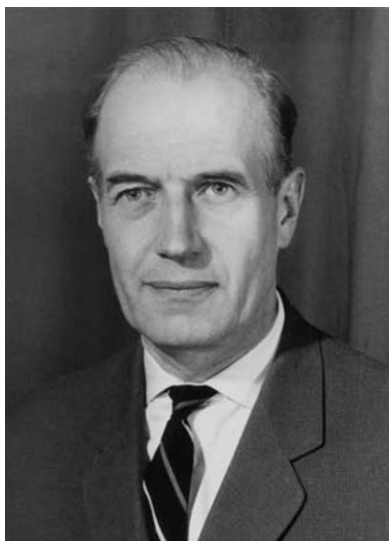


Figure 1. N.D. Sokolov (1912–2002)—the last graduate student of Hans Hellmann (Figure 25). For decades he served as the main organizer of the Quantum Chemistry Meetings in the USSR. (Thanks to the photoarchive of the Semenov Institute of chemical Physics RAS, Moscow, Russia, for the kind permission to publish this photo).



Figure 2. V.A. Fock (1898–1974). Inventor of the HF method, of whom it was known that 'Fock kann einen Stiefel ausrechnen'. (Fock can integrate a boot';—P. Ehrenfest; Thanks to the family Fock for the kind permission to publish this photo).



Figure 3. I. Kant (1724–1804). Since 1770 professor in the Königsberg (Now Kaliningrad, Russia; Korolewetz is the ancient Russian name for this city) University bearing his name now. In 1758 the city undergoes to the Russian jurisdiction (until 1762) during the Seven Year's War. The application (1758) to the Empress Elisabeth of Russia for an ordinary professorship had been rejected. That easy eternal enemies are made. Portrait (1768) by Becker (1720–82) is in Schiller-Nationalmuseum, Marbach am Neckar, Germany. (Source: Wikimedia).

What a light can mathematics ignite in the spagirc science,⁵ can only one foresee who is initiated in it and knows such chapters of natural science happily treated mathematically like hydraulics, aerometry, optics et al.: all what was obscure, doubtful, and unreliable, mathematics made clear, trustworthy, and obvious. Many, however, deny the possibility to put principles of mechanics in the foundation of chemistry and ascribe it to sciences... If those who obscure all their days with smoke and soot and in whose brain the chaos reigns from the mass of unreasoned experiments not shun to learn sacred laws of geometers which have been once rigorously established by Euclid ..., they for sure could deeper penetrate into mysteries of Nature ... Indeed, if mathematicians comparing a very few lines derive very numerous truths then I do not see any other reason why chemists could not derive more laws from that abundance of available experiments, except ignorance of mathematics.

After that Lomonosov declares an intention to present chemistry axiomatically: never fulfilled because of other duties—the situation well familiar to everybody. Despite the quite scholastic flavor of the old fashioned text it goes about setting out a logical—vis. reference to Euclid—geometrical structure for describing chemical phenomena rather numerics with which Kant seems to be more concerned. This is even more remarkable since Lomonosov himself (according to Rus-

sian/Soviet tradition) is much more known as an ardent champion of *quantitative*, that is, numeric approach which was not dominating in chemistry of the XVIII century. Nevertheless, the attitude to the subject demonstrated by Lomonosov shaped certain intellectual atmosphere where the idea of a deep mathematical structure inherent for chemistry was very natural.

Origin of iconic language

The divergence between chemical and physical pictures of molecular structure is well documented and described as that between “symbolic and iconic representations”.^[9] In this subsection we are going to trace the origins of this divergence in the motion of the focus chemists and physicists had in respective periods of time. With such an introduction nobody will be surprised if we recollect the personage of Figure 5 who only ca. 2050 years ago wrote:^[10]

*dicere enim possis caelestem fulminis ignemp
subtilem magis e parvis constare figuris
atque ideo transire foramina quae nequit ignis
noster hic e lignis ortus taedaeque creatus.
praeterea lumen per cornum transit, at imber
respuatur. quare, nisi luminis illa minora
corpora sunt quam de quibus est liquor almus aquarum?
et quamvis subito per colum vina videmus
perfluere, at contra tardum cunctatur olivom, aut quia ni mirum
maioribus est elementis
aut magis hamatis inter se perque plicatis,
atque ideo fit uti non tam diducta repente*



Figure 4. M.V. Lomonosov (1711–1765). With some stretch the *in absentia* discussion between Kant and Lomonosov may be considered as one between two Russian scientists (or two German ones since Lomonosov returned to Russia only in 1741, and it is not clear where the manuscript^[8] had been compiled). The only *intravital* portrait by G. Prenner conserved in the Lomonosov Home-Museum, Ust-Ruditsa, Russia. (Source: Wikimedia).

⁵Chemistry is meant.

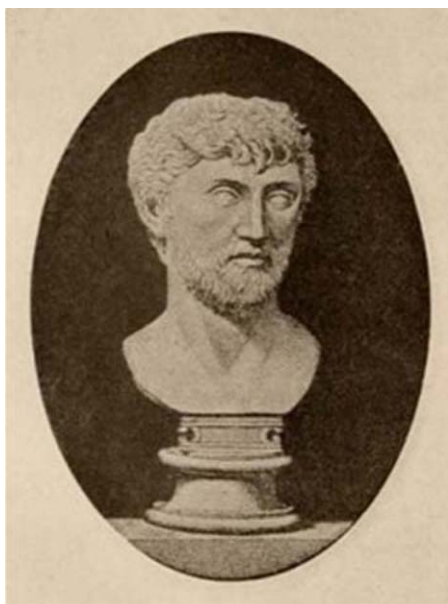


Figure 5. T. Lucretius Carus. (ca. 99–ca. 55 BC). (Source: Wikimedia).

*inter se possint primordia singula quaeque singula per cuiusque
foramina permanere*

*Huc accedit uti mellis lactisque liquores
iucundo sensu linguae tractentur in ore;
at contra taetra absinthii natura ferique
centauri foedo pertorquent ora sapore;
ut facile agnoscas e levibus atque rutundis
esse ea quae sensus iucunde tangere possunt,
at contra quae amara atque aspera cumque videntur,
haec magis hamatis inter se nexa teneri
proptereaue solere vias rescindere nostris
sensibus introituque suo perumpere corpus.
omnia postremo bona sensibus et mala tactu*

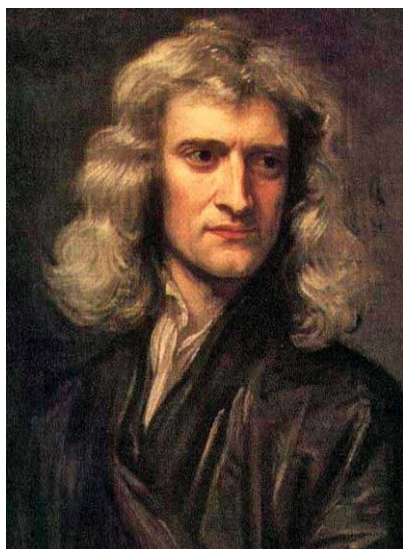


Figure 6. Sir Isaac Newton (1642–1726/7). Portrait (1689) by G. Kneller (1646–1723). (Source: Wikimedia).



Figure 7. C.L. Berthollet (1748–1822). (Source: Wikimedia).

which in the κοινῇ of today sounds like:

*thus the fire of lightning can pass where earthly fire cannot,
because it is formed of finer atoms: for like reasons light passes
through horn, rain does not; wine runs easily, oil slowly through
a strainer, because the elements of oil are larger or more hooked,
and so cannot separate so readily.*

*honey and milk are pleasant to the taste, wormwood and the
like nauseous; the former therefore consist of smooth, the latter
of jagged atoms which tear a way into the body.*

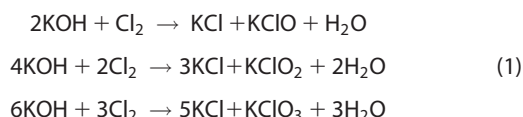
For us the most important idea in the above passage is that, if something holds together, there has to be *some other thing*, which keeps together the parts. Some mechanical hook or support seemed to be necessary. Apparently the hooks could be drawn and their consecutive entanglements produce a topological structure. Also an idea that each sort of atoms can possess sort-specific numbers and kinds of hooks looks pretty natural, but seems to be never articulated.

The break with the concept of mechanical support or hook is due to personage of Figure 6.^[11] The largest object available for observation that time: the Solar System, composed of clearly visible parts staying together, and the course of the Sun and planets, was explained not through crystal spheres which for thousands of years seemed to be necessary to maintain the celestial order, but through an absolutely new agent: “gravitational attraction, an invisible force able to act over vast distances”—a field.

The idea of field penetrated chemistry due to personage of Figure 7 and had a remarkable correspondence with his activity as a practicing, moreover, as a *technical* chemist. Working on chlorine bleaching, which made him a *Comte d’Empire*, the title under the Restauration (after a short Russian excursion to Paris) enhanced to “*Pair de France*,” he dealt with the processes in the today notation described by *brutto* relations:



Figure 8. J.-L. Proust (1754–1826). (Source: Wikimedia).



and arrived to a wrong conclusion that the composition of the product depends on the amount of the reactants used. Apparently, he had no reliable means to distinguish white powders KClO_n ; $n=1\div 3$, yielded in different proportions from the processes eq. (1). Taking this as an experimental fact he dared suggest that atoms are held together by forces similar to gravitational ones. This is a very logical conclusion from the above wrongly understood experiment: there is no obvious limit of the number of bodies (either atoms or planets) which could be held together by an attractive field. The distinction between the two viewpoints (field and hook) is more than distinct: fields are not saturable, whereas hooks are.

The idea of dependence of the composition of an individual substance on the preparation conditions and amount of ingredients has been opposed by the personage of Figure 8. The outcome of the discussion was that the “regular” chemical



Figure 9. J. Dalton (1766–1844). Etching (1834) by Charles Turner (1773–1857) after James Lonsdale (1777–1839). (Source: The Library of Congress).



Figure 10. Sir Edward Frankland (1825–1899). (Source: Wikimedia).

compounds for convenience called *daltonides* to celebrate the personage of Figure 9 have composition with some fixed proportions between different *elements*.[†] For the compounds of definite composition the affinity force holding atoms together turned out to have a discrete character which brought the chemistry into a specific position relative to the Newtonian picture of Nature based on continuous functions. It turned out to be discrete not only in terms of involved agents (atoms); the interactions among the agents turned out to be discrete as well—quite a strange situation contrary to the uniformity and continuity of the forces known that time in physics. The necessity to represent quite unusual relations between components had been formalized in the concept of valence due to the personage of Figure 10. The idea itself was nothing, but fixing the number of hooks belonging to each type of atoms. Systematic usage of the rules that each hydrogen atom has one and only one hook, oxygen—two, and carbon four and only four, together with the allowance to atoms to be connected by several pairs of hooks led in the subsequent years by the efforts of Gerhardt, Laurent, and finally of Kekulé (Fig. 11) and Boutleroff (Fig. 12) to a development of a very specific language: fairly topological and pictorial (iconic) which is habitually confronted to the symbolic language of physics.**

Considering the process in a more abstract way one can say that the events developing in chemistry in the end of XVIII—beginning of XIX centuries were those which H. Weyl^[12] later called *coordinatization*, that is, mapping of a set of objects

[†]An opposite situation is also possible as established on purely topological grounds, and the term “berthollide” was coined to describe it, (Kurnakov, Z. Anorg. Chem. 1925, 146, 69) but exploring this branch would lead us too far. Next time.

^{**}It is now a common place to confront the symbolic language of physics with the iconic language of chemistry. This confrontation is in a way artificial and portrays chemists as complete idiots not able even to read a normal (Western) text since in it the sounds are represented as *symbols*. It is not the case, and even more: about the same time chemistry went through a shift from an *iconic* notation for elements used yet by Dalton visually not that much different from the archaic *alchemical* notation to the modern *symbolic* one by Berzelius.

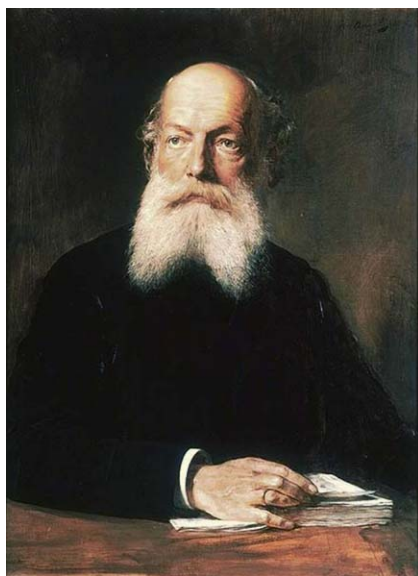


Figure 11. F.A. Kekulé von Stradonitz (1829–1896). Portrait (1890) by H. von Angeli (1840–1925). Alte Nationalgalerie, Berlin, Germany. (Source: Wikimedia).

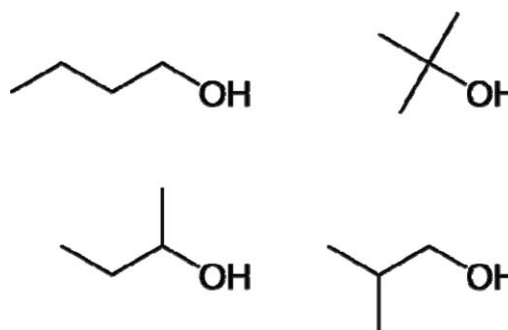


Figure 12. A.M. Boutleroff (1828–1886). Original by Anonymous conserved in the Museum of the Kazan State University, Kazan; Russia.

upon a set of “reproducible symbols”—coordinates. In the most general sense it goes about ascribing names (coordinates) to objects (points). The notation of eq. (1) characterizes only the composition of a molecule. The examples available that time belonged largely to the realm of *inorganic* chemistry. It was going about relatively simple oxides, salts, acids, and bases. For these compounds the composition was sufficient to identify them completely. It is not the case for “organic” molecules. A larger set of coordinates is needed to establish a one-to-one correspondence between points (molecules) and reproducible symbols, serving as coordinates in their “space” which turned out to be (colored) graphs.^{†† [13]} Boutleroff’s fundamental result was to experimentally produce a proof that each of four structures in Scheme 1 indeed represents an individual alcohol. The quotation is quite remarkable: “Assuming that each chemical atom possesses only a definite and limited amount of chemical force (affinity), with which it takes part in forming a body I would call chemical structure ... a way of mutual connection of atoms in a composite body...”. “... for each [chemical] body only one rational formula will be possible, and when the general laws expressing the chemical properties of the [chemical] bodies on chemical structure become known, that formula will express these properties.”^[14] It is absolutely clear that it was going about establishing a one-to-one correspondence between molecules and colored graphs.^{‡‡} This corre-

spondence works for more than a century as a language for organic chemistry able not only to *name* fairly weird compounds (Scheme 2) but also to describe and design their reactions (Scheme 3) without any reference to what are the sticks.

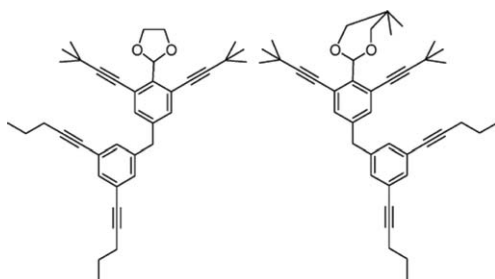
The obvious formal character of so emerged language naturally brought to the idea to make a step further and to formulate and prove theorems of chemistry. Taking the axioms of the theory of colored graphs as those for chemistry allows one to derive Boutleroff’s result about the number of possible butyl alcohols or that of alkanes. The statement that there are three and only three pentanes—connected graphs formed by five four-valent and twelve monovalent vertices looks out as a pretty solid *theorem* of chemistry despite known skepticism concerning the possibility of such theorems at all.^[15] More general statements of that type—enumeration of the alkane isomers as function of the number of carbon atoms (paper communicated by C. Schorlemmer, wrong author’s initial: E. Cayley instead of A. Cayley ...) ^[16] so forth—are due to personage of Figure 13. What seems not to be good is the starting point: the graph theory itself. Not because it is anyhow inherently bad, but because doing so shrinks the playground to pure combinatorics. If one says “molecule is a graph” the only



Scheme 1.

^{††}H. Weyl was not very clear writing about the coordinatization. Although he states the opposite, no clear example of “coordinates” which would be of non-numerical nature is given by him. Shafarevich (И.Р. Шафаревич, Основные понятия алгебры (I.R. Shafarevich, *Basic concepts of algebra*) Izhevsk, 1999) gives necessary examples of non-numerical coordinates explicitly.

^{‡‡}In fact Boutleroff goes further and suggests an existence of “a mathematical theory of molecular force called chemical affinity” to be based on/derived from these graphs. He also takes for granted that the “affinity” is “quantized”: not only “definite and limited”, but also that only an integer amount of affinity can be ascribed to an atom and spent for bonding by integer amounts.



Scheme 2. Reprinted (adapted) with permission from (Chanteau and Tour, J. Org. Chem. 2003, 68, 8750. DOI: 10.1021/jo0349227). Copyright (2003) American Chemical Society.

thing which remains is to derive respective combinatorial formulae, which is largely done yet by Cayley, but is getting improved until now.^[17]

Behind the language

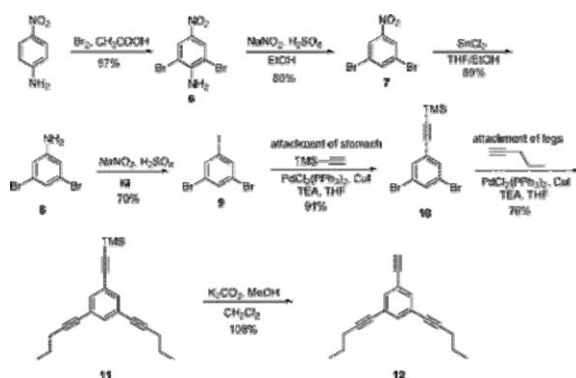
The efficiency of the chemists' mother language is enormous. Everyone who, like the present author, is not in a full command of it always confronts with the question "why?" Why and when molecule can be represented by a graph? An extreme viewpoint is that everything can be called by whatever name, and these names can themselves bear other names^[18] *ad infinitum*. So, why not a graph? However, relation between molecules and graphs has to be material otherwise there would be no grounds for events depicted in Scheme 3 to happen with the substances taken from pots on the shelf bearing etiquettes with the graphs naming reactants. For this some reality has to hide behind these pictures. Which one? An impatient reader can already say "I know!," but, wait, what you, probably, know stands still many decades in the future as related to the chemical-mathematical story to be told now.

Molecules and Invariants. The Cayley enumeration of alkanes fairly deserves the qualification of a topological statement, even a theorem, about chemistry. To understand what did actually happen we have to ask two questions: what did Cayley actually do and why? The answers are pretty unexpected: he had no intention to calculate the number of isomers—it was a by-product. Cayley counted the number of graphs with

a fixed number of arcs incident to a node ("valence"). But what he wanted to count was the number of "invariants." They were a topic actively studied by British mathematicians in the second half of the XIX century.^[19] Invariant of a function (form) J of a vector (x,y) is an expression which under substitution:

$$\begin{aligned}x' &= \alpha x + \beta y \\ y' &= \gamma x + \delta y\end{aligned}\quad (2)$$

transforms as $J' = (\alpha\delta - \gamma\beta)^{\lambda} J$ and similarly for the forms (polynomial functions) of larger number of vector arguments—see below. In the middle of 19th century the invariants had been sought in a way sporadically and each found invariant was an independent discovery. Thus, the heuristic idea due to personage of Figure 14 was very handy: it allowed one to construct new invariants more or less systematically by drawing the pictures according to the formal rules of "valence":^[20] "The factors of any algebraical form may be regarded as in some sense the analogues of the rays of atomicity in the equivalent chemical atom these rays being what Dr. Frankland, according to his nomenclature, would have to designate as free bonds; such rays between two consecutive atoms in a molecule are conceived as blending in some manner so as to represent some unknown kind of special relation existing between them; they may then with propriety be called bonds or lines of connexion." Today the quotation calls for an explanation. Mathematically a "ray" is an object derived from a vector $\mathbf{v} = (x,y)$ by multiplying it by all possible positive factors λ . The *bond* $(\lambda_1 \mathbf{v}_1, \lambda_2 \mathbf{v}_2)$ is, thus, something which does not depend on λ_1, λ_2 . It is a matter of mathematical technique to replace real positive λ 's by complex ones and to generalize the scaling to an arbitrary linear transformation eq. (2). In this extended setting Sylvester's *bond* is a



Scheme 3. Reprinted (adapted) with permission from (Chanteau and Tour, J. Org. Chem. 2003, 68, 8750. DOI: 10.1021/jo0349227). Copyright (2003) American Chemical Society.

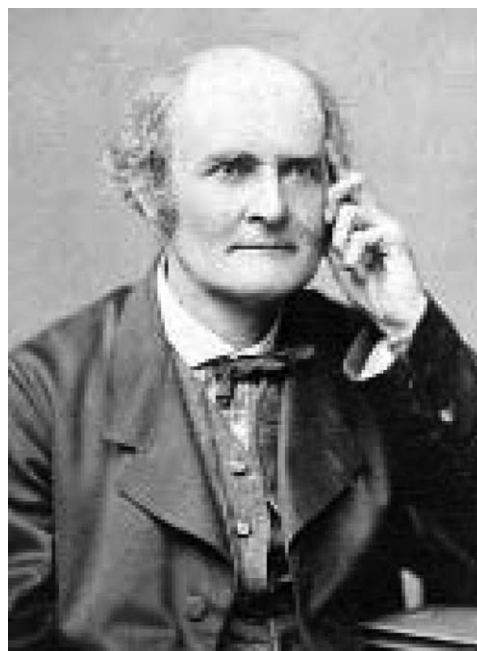
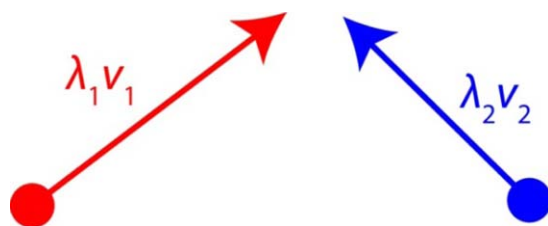


Figure 13. A. Cayley (1821–1895). (Source: Wikimedia).



Figure 14. J.J. Sylvester (1814–1897). (Source: Wikimedia).



Scheme 4.

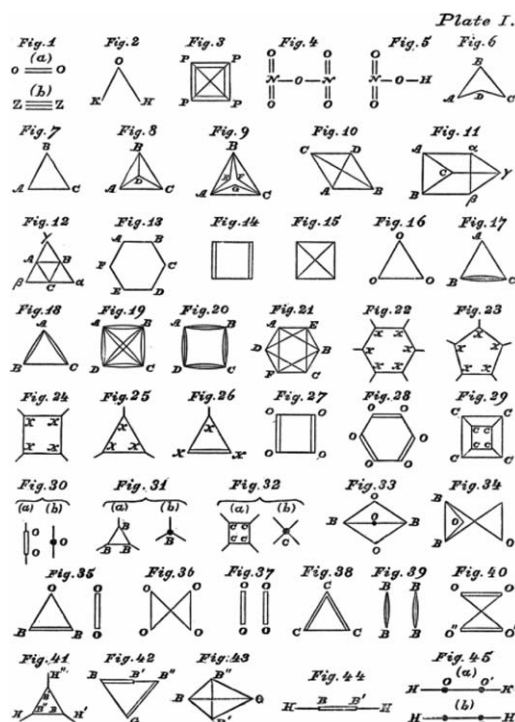
function of two two-dimensional vectors which remains unchanged (invariant) under the transformation:

$$\begin{aligned}x'_i &= a_i x_i + b_i y_i \\ y'_i &= c_i x_i + d_i y_i\end{aligned}\quad (3)$$

with $a_i, b_i, \dots \in \mathbb{C}; i=1, 2$.^{§§} Sylvester was fascinated by the opened possibility of constructing invariants and produced quite an amount of them (Fig. 15). The natural (mathematical) question was how many invariants can be constructed with use of these pictures and that was the question Cayley answered.^[15] Like in the case of the Kant–Lomonosov “controversy,” the chronology should not deceive us. The fact that Cayley’s publication,^[15] where the invariants and graphs are counted, appeared before one by Sylvester^[20] does not mean that the idea was not communicated in that or other way. Sylvester^[20] rather bitterly complains that a reference to his contribution somehow disappeared from Ref. [15].

Invariants and Molecules. Sylvester’s heuristic approach eventually turned unnecessary with the introduction of the symbolic method which allowed to reduce the calculation of

^{§§}If $\det \Omega_i = 1; \Omega_i = \begin{pmatrix} a_i & b_i \\ c_i & d_i \end{pmatrix}$ then $\Omega_i \in SL(2, \mathbb{C}) \supset SU(2)$ and $SU(2)$ is the group of electronic spin.


 Figure 15. Sylvester’s pictures used to produce invariants. (Reproduced from Sylvester, *Am J Math*, 1878, Vol. 1, pp. 64–104 © Johns Hopkins University Press, courtesy of JSTOR).

invariants to a kind of systematic mechanical process (see Ref. 19 for more detailed account). In relation to chemistry it led to a “checkerboard turnaround,” that is, to a shift of the focus: not the structural formulae of chemistry served as a (heuristic) source of new invariants for mathematics, rather the operations of the symbolic invariants theory applied to polylinear forms generate structural formulae of chemistry.^[21] This shift of the focus arose from quite a remarkable collaboration between the King of Invariants theory (Fig. 16) and a Don cosack, graduate of the Moscow University, later professor and rector in Jurjew/Derpt/Depart, the founding rector of the Voronezh State University in 1918, and after that privat-dozent in Tartu^{¶¶} University (Fig. 17).^[22] Although the mathematical part of this joint work was very much influenced by P.A. Gordan and lays perfectly in the line of the symbolic method of the invariants theory, the chemical application roots in a school of thinking specific for Russia of that time: The Moscow philosophical-mathematical school^[23] which promulgated a version of arithmology—an extension of the Leibnitz monadology. As we mentioned previously the predominant mathematical technique of the XIX century as applied to natural sciences was based on (partial) differential equations. These results in quite a rigid picture of the reality: its evolution is uniquely predefined by initial conditions. The way of thinking stemming from a (quite nonchalant) generalization of these results of the mathematical physics of XIX century was considered as an oversimplification by the Moscow philosophico-mathematical

^{¶¶}Tartu is the Estonian name of the city for which Jurjew (pronounced [ju:rlʲɛf]), Derpt, and Depart are respectively Russian, German, and Swedish names.



Figure 16. P.A. Gordan (1837–1912)—King of the Invariants theory; known to physicists and chemists for the Clebsch-Gordan coefficients in the theory of angular momentum. (Source: Wikimedia).

school which, by contrast, stressed the importance of discreteness, discontinuity, and stochasticity particularly for social extensions. Chemistry represented by its formal atomistic and valence aspects seemed to be a good playground for discussing discreteness on the own soil of natural sciences. Alexejeff belonged to this school and his intention was also to provide the mathematical background to the very successful language of (organic) chemistry which otherwise used only extremely primitive primary school mathematics in contrast to the elaborated and refined one used in mathematical physics. I would dare say that this group of scientists, although being led by very peculiar philosophical concepts (at least from the contemporary point of view), was able to receive very early signals from the quantum world sent to humans and was trying to adequately process these signals. Identifying the free valences of each atom with linear functions of components of 2D vectors and applying so called convolution (*Faltungsprozess*) taken from the symbolic invariants theory to pairs of two such functions produces an expression—bracket factor (*Klammerfaktor*)—an invariant. Although, the convolution was defined in terms of standard mathematical operations like differentiation, it can be also performed in a “graphical mode.” Namely, denoting a linear function(al), as $a \rightarrow$, bilinear ones as $\leftarrow b_1 \rightarrow$ and/or $\leftarrow b_2 \rightarrow$ etc. (with the arrows reminiscent of vectors in Scheme 4)—the notation practically identical to the contemporary one—the formation of the bracket factor in the graphical mode consists in replacing two involved arrows each by a valence dash:

$$\begin{aligned} a \rightarrow \leftarrow b &\Rightarrow a-b \\ a \rightarrow \leftarrow b \rightarrow &\Rightarrow a-b \rightarrow \\ \leftarrow b_1 \rightarrow \leftarrow b_2 \rightarrow &\Rightarrow b_1=b_2 \end{aligned} \quad (4)$$

The similarity to the structure formulae of organic chemistry is obvious. Identifying linear forms with monovalent, bilinear ones with divalent etc atoms established not only the one-to-one correspondence between the structure formulae of organic chemistry and invariants of the polylinear forms of the 2D vectors (Fig. 18), but also with the generalized isomeriza-



Figure 17. V.G. Alexejeff (1866–1943(?)). That is how a Russian professor looked like 100 years ago. (Source: Wikimedia).

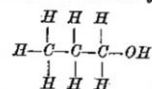
tion processes—actually that of a chemical transformation—could be expressed in terms of the operations defined in the symbolic theory of invariants. This established the equivalence between *iconic* and *symbolic* languages of chemistry. Their difference is indeed secondary although their purely visual contrast being factually immaterial is repeatedly stressed.^[9] Accepting that or another form is a matter of convenience in that or another situation and even more: merely a matter of habit. Curiously enough, namely the equivalence of two languages served as a ground for rather harsh criticism^[24] of the work.^[21] It seemed that it went merely about a translation “from German to French.” Of course, that time the tentative usefulness of invariants for chemistry was very hypothetical. From our today perspective a statement that an isomer is a function (invariant) has much more credibility than it could be imagined in 1901.

New brave quantum world

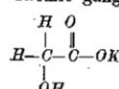
The results^[21] had been acquired without knowing neither anything about what is a wave function (WF) or the quantum theory itself even in its elementary form; that electrons have anything to do with bonding (although an intimate, but obscure relation between electricity and chemistry had been known since the times of Sir H. Davey), and so forth. It was a triumph of purely formal mathematical thinking in a pretty much *a priori* manner.

Spin-valence Intermezzo. Subsequent events seem to be better known to the public. The facts that a hydrogen atom contains one electron and that further atoms’ chemistry is better characterized by the atomic number—that of electrons rather by the atomic weight (as Mendeleev originally thought) had been established. The Lewis idea that chemical bond is formed

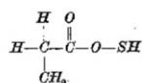
Dio Formeln, wie sie bis jetzt in der Chemie gangbar waren:



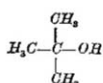
Propylalkohol, (C_3H_8O)



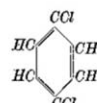
Kaliumglykolat, $(C_2H_5O_2K)$



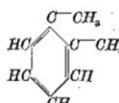
Amidothiacetsäure, $(C_2H_5O_2SN)$



Tertiärer Butylalkohol, $(C_4H_{10}O)$



Paradichlorbenzol, $(p-C_6H_4Cl_2)$



Orthodimethylbenzol $(o-C_6H_4)$

$C = c_x c_x c_x = c_x^3$, $H = h_x$, $O = o_x o_x = o_x^2$, $Cl = cl_x$
 Kohlenstoff Wasserstoff Sauerstoff Chlor
 $K = k_x$ Kalium, $N = n_x n_x = n_x^2$ Stickstoff u. s. w.

Unsere obigen Formeln nehmen in der neuen Bezeichnung folgende Form an:

$(c_1 c_2)(c_3 c_3)(c_1 h)^3(c_3 h)^3(c_3 o)^3(o h)$
 Primärer Propylalkohol,

$(c_1 c_3)(c_1 h)^3(c_1 o)(o h)(c_2 o_1)^3(c_3 o_2)(o_2 k)$
 Kaliumglykolat,

$(c_1 c_2)(c_1 h)^3(c_1 n)(n h)^3(c_2 o)^3(c_2 o_1)(o_1 s)(s h)$
 Amidothiacetsäure,

$(c_1 c_3)(c_1 c_3)(c_1 c_4)(c_3 h)^3(c_3 h)^3(c_4 h)^3(c_1 o)(o h)$
 Tertiärer Butylalkohol,

$(c_1 c_2)(c_2 c_3)^3(c_3 c_4)(c_4 c_5)(c_5 c_6)(c_6 c_1)^3(c_1 c_1)(c_2 h)(c_3 h)(c_4 c_1)(c_5 h)(c_6 h)$
 Paradichlorbenzol,

$(c_1 c_2)(c_2 c_3)^3(c_3 c_4)(c_4 c_5)(c_5 c_6)(c_6 c_1)^3(c_1 c)(c h)^3(c h)^3(c_5 h)(c_4 h)(c_6 h)(c_6 h)$
 Orthodimethylbenzol.

Figure 18. Correspondence between iconic and symbolic languages in organic chemistry the latter incidentally being the electronic WF. (Adapted from "Übereinstimmung der Formeln der Chemie und Invariantentheorie" Gordan and Alexejew, Z. phys. Chem. 1900, 35, 612).

when electrons make a pair—the description having fair analogy to either entanglement of hooks or to *Faltung* of linear multipliers of the polylinear forms. The key step was the recognition of the "doubleness" of an electron^[25] which technically converted into the two-dimensionality of the linear form representing ones state*** and ascribing the determinant form to the WF of two electrons identified with the Lewis electronic pair:^[26]

$$\begin{vmatrix} \alpha'(s_1) & \alpha'(s_2) \\ \beta'(s_1) & \beta'(s_2) \end{vmatrix} \quad (5)$$

with

$$\begin{aligned} \alpha' &= a\alpha + b\beta \\ \beta' &= c\alpha + d\beta \end{aligned}$$

Inserting the linearly transformed spin functions of individual electrons in the determinant we conclude that the linear transformations result in the numerical factor $(ad-bc)$ —that is, the function eq. (5) is an invariant.

The formal equivalence with the construct^[21] was fairly recognized by the authors (Figure 19),^[26] but it never appeared in the subsequent publications. Even in the "Theory of Spinors"^[26e] published in the USSR, which contained the entire chapter devoted to the theory of spin-valence, the earlier works^[21] have not been mentioned.

Culmination. We see that by the year 1930 the entire (now quantum) theory behind chemical language together with the necessary prerequisites for numerical implementation seemed about to be ready. The famous Dirac's quotation^[27] reflects this optimistic attitude: "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". Moreover, Lomonosov's program of axiomatic (re)construction of at least a good portion of chemistry had been almost performed. Indeed, the Carathéodory axioms of thermodynamics^[28] supplied by the standard relation between the thermodynamic quantities and the potential energy surface (PES) eventually contains a large part of chemistry and is thus its fair axiomatic. Specification of the molecular electronic Hamiltonian:

$$\begin{aligned} H = & -\frac{1}{2} \sum_i^N \frac{2}{r_i} + \frac{1}{2} \sum_{\alpha\beta}^A \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} \\ & + \frac{1}{2} \sum_{ij}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{\alpha i}^{AN} \frac{Z_\alpha}{|\vec{R}_\alpha - \vec{r}_i|} \end{aligned} \quad (6)$$

for a system of N electrons in the electrostatic field of A nuclei (labeled, respectively, by i 's and α 's) together with the nuclear repulsion potential yields the expression for the PES:

$$E(\{\vec{R}_\alpha\}) = \min_{\Psi} \langle \Psi | H | \Psi \rangle \quad (7)$$

involving the electronic WF:

$$\Psi = \Psi(\{\vec{R}_\alpha\} | \{x_i\}),$$

where $x_i = (\vec{r}_i, s_i)$; with s_i being two-valued spin-projection variable finalizes the construct (axioms of quantum mechanics complemented by the Pauli principle which is an independent statement^[29] are assumed to be added as well).

Nevertheless, the problem remains: Cayley's statements about the number of isomeric alkanes must be derivable from this axiomatics. The corresponding (proto)theorem may sound somehow like: "For alkanes⁺⁺⁺—the family of Schrödinger

***A (spin) state of an individual electron is given by the linear form $a\alpha(s) + b\beta(s)$ with normalized a and b .

+++hydrocarbon of the general formula C_nH_{2n+2} .



Figure 19. F.W. London (1900–1954) (publishes with a permission of the AIP Emilio Segrè Visual Archives, Physics Today Collection), W.H. Heitler (1904–1981) (Source: Wikipedia), H.K.H. Weyl (1885–1955); photo (ca. 1928) by Franz Schmelhaus (ETH-Bibliothek Zürich, Bildarchiv) and Y.B. Rumer (1901, Moscow—1985, Novosibirsk) thanks for the permission of Prof. K. Kikoin (Jerusalem, K.A. Кикоин, По обе стороны свободы, “Филобиблон”, Иерусалим, (K.A. Kikoin, On either side of freedom, «Philobiblon», Jerusalem) 2011 [in Russian].)—creators of the theory of spin-valence—the forerunner of the valence bond theory.

equations with $Z_\alpha = 6$ for $\alpha = 1 \div n$; $Z_\alpha = 1$ for $\alpha = n + 1 \div 3n + 2$, so that the entire number of nuclei $A = 3n + 2$ and the number of electrons $N = 8n + 2^{+++}$ and $n = 5$ —the number of distinct minima—up to the transposition of the equivalent nuclei and simultaneous three dimensional translations and rotations of all vectors $\{\vec{R}_\alpha\}$ —on the ground state PES equals exactly to three.” The Cayley enumeration formula must be derivable as well for the entire family of the Schrödinger equations giving the number of PES minima for arbitrary n . In other words, the statement about the number of minima must be proven for the family of functions Ψ satisfying the family of Schrödinger equations:

$$H\Psi = E\Psi \quad (8)$$

partial differential ones of second order (due to ∇_i^2 's) of $3N$ spatial variables in each point $\{\vec{R}_\alpha\}$ of the nuclear configuration space. It is hardly believable that the available methods of mathematical physics are able to provide any statement of that kind without additional assumptions. The quotation,^[27] however, goes further and says: “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.” This part of the quotation is very frequently neglected since today people tend to say something like “in our days the computer power allows what had not been available to Dirac.” However, no computer power is able to prove general statements about molecules, like Cayley enumeration or whatsoever. Dirac can hardly be understood that way, that it indeed goes about “approximate practical ... computation.” The key word is “explanation,” but it requires some instrumentation. Not the numerical tricks are meant, but a fair theory. Taking the WF Ψ as a product of spin-invariants has to be either postulated as an additional assumption

⁺⁺⁺equal to the sum of all nuclear charges.

(axiom) or externally justified, but in either case it makes the business. The colored graphs—coordinates in the space of molecules turn out to be their electronic WFs which can be used to estimate PES eq. (7). Of course, the question “why?” remains unanswered, but the tentative power of such an axiomatics overweighs the concerns about its basics. On the other hand any attempt to prove that Ψ must have the form prescribed by the theory of spin-valence or establish the conditions when it is possible eventually contributes significantly to the mathematical theory of chemistry.

Rivalry, Fuzziness, Vagueness, or Why Everything Went Wrong?

After the brilliant culmination of 1930s theoretical chemistry had to go from one triumph to another and it was actually so for a while. Nevertheless, as we can read now^[3] the current situation is far from harmonic: people complain about fuzziness and instability of their concepts, about absence of unifying viewpoint, so forth. Doubts are raised again concerning the possibility of theorems of chemistry, so that we in a way find ourselves back in the Kantian epoch. The future appearance of these problems had been predicted yet at a very early stage^[30] and had been ascribed to disproportionate reliance on numerical experiment. In this section, we shall try to identify the sources of the outlined problems which lay incidentally in the diversity of the physics of complex electron-nuclear systems, but also in some deficiencies of the theoretical approaches used so far.

MO or VB? VB and MO, and all, all, all...

Despite some revival^[31] of the VB in the last decade the quantum chemistry of today is by 99% percent dominated by the molecular orbital (MO)-based methods. Such an inclination toward obviously numerically less efficient (at least $O(N^3)$ vs $O(N)$ scaling) and less intuitive approach—try to imagine how to prove the Cayley's enumeration formula taking Ψ as a Slater determinant

constructed on occupied MOs—must have some grounds except human imperfection. The divergence between two intellectually attractive theories was, nevertheless, a basis of an involved discussion^[15] a conclusion of which was that, in principle, there is no contradiction between the two. The same is stressed in Ref. [9]. This conciliating conclusion about the nonexistence of any rivalry between the MO and VB pictures is based on “existence theorems” stating that the expansion of the exact WF over the complete functional basis set can be obtained irrespective to the type of the expansion term taken first. It may be either a single Slater determinant built of MOs or a VB, or whatever another WF; this choice is immaterial as far as we are able to have eventually infinite expansion. There is no doubt that in the infinity we all shall be rich and happy. We live, however, not in the infinity, but here and now so that the question what first term is going to give us a shorter expansion (from the numerical point of view) or by itself gives a better description of the ground state is a legitimate one. Moreover, as Fock noticed^[32] (see also Ref. [33]) the approximations reasonably approaching and qualitatively reflecting the characteristic features of the exact solutions of the Schrödinger equation generate qualitative concepts bound to this approximation. The answer to the question of its quality based on that or another first term is incidentally the answer to the question which concepts are better.

Setting an example. We shall analyze these issues on the simplest possible example: that of the H₂ molecule modelled by the Hubbard Hamiltonian (Fig. 20): comprising one-electron hopping t between two 1s-orbitals (which decays exponentially fast with increase of the internuclear separation), and the one-site repulsive potential U being the simplest simulation to the Coulomb interaction between the electrons—the pet of Russian theoreticians of more recent times (Figs. 21 and 22) which we supplied by a nuclear repulsion term in order to make curves more chemically looking. The Hartree–Fock (HF) WF built upon the *symmetric* MO LCAO

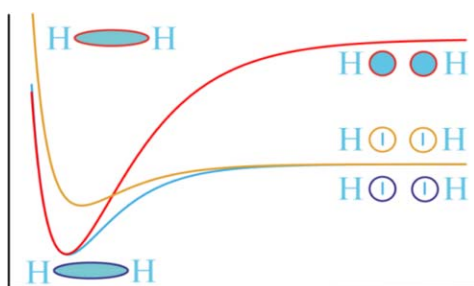


Figure 20. Energy profiles for the H₂ molecule modelled by the Hubbard Hamiltonian in various approximations. Color coding: red—the energy profile derived in the HF approximation; beige, in the HL one, blue—“exact” solution. We also illustrate the significant dispersion of electrons’ numbers in AOs by filling the ellipses or the circles. In the HF state electrons’ numbers on either side are uncertain although the *averages* of the electron numbers *operators* remain unity. At the infinite separation the HL function becomes that of two isolated H atoms forming the singlet state. Electrons are shown as vertical dashes to stress that the dispersion of the numbers of electrons is vanishing in this case. The usual arrows are dropped as the electrons do not have definite spin projection: the average is vanishing, but the dispersion is large as each of electrons can have either of two opposite values of it: $\pm \frac{h}{2}$.



Figure 21. I.A. Misurkin (1934–2013). (Thanks for the kind permission of Prof. Dr. T.S. Zhuravleva).

$$|s_{\uparrow}s_{\uparrow}|$$

$$s(\vec{r}) = \frac{1}{\sqrt{2(1+S)}}(l(\vec{r}) + r(\vec{r})) \quad (9)$$

$$l(\vec{r}) = \varphi(\vec{r} - \vec{R}_l); r(\vec{r}) = \varphi(\vec{r} - \vec{R}_r)$$

(S is the overlap integral between the orbitals centered on the left (l) and right (r) ends of the H₂ molecule; $|\dots|$ stand for the Slater determinant—spin-invariant—of the enclosed spin-orbitals) is the exact answer of the electronic problem with vanishing interaction ($U = 0$). For the symmetry reasons it will remain the solution of the HF electronic problem *irrespective* to the values of t and U . Performing what today is called the



Figure 22. A.A. Ovchinnikov (1938–2003). In variance with^[12] he used to say “Quantum chemistry is a part of theoretical physics.” (Thanks for the kind permission of Prof. Dr. M. Ya. Ovchinnikova).

"VB reading" of this WF shows that it is (always) equally contributed by the Heitler–London (HL) WF:

$$\frac{1}{\sqrt{2(1+S^2)}}(|r_{\downarrow}l_{\uparrow}|+|l_{\downarrow}r_{\uparrow}|) \quad (10)$$

and by the "ionic" state, where either of two orbitals is doubly occupied:

$$\frac{1}{\sqrt{2(1+S^2)}}(|r_{\downarrow}r_{\uparrow}|+|l_{\downarrow}l_{\uparrow}|) \quad (11)$$

In the limit of the infinite interatomic separation the energy must flow to that of two isolated hydrogen atoms (zero), but it is not the case: it flows to $U/2$ to the half of the interaction energy of two electrons occupying the same orbital (red curve). This is obviously wrong and this is the fundamental defect of the HF approximation: overestimation of the weight of the ionic configurations (in this example it is constant $1/2$ irrespective to the parameters' values/molecular geometry). The correct answer in the infinite separation limit is also known: this must be two isolated hydrogen atoms, forming a singlet state; it is nothing, but the HL function itself eq. (10). The corresponding energy profile is given by the beige curve.

It does not represent any problem to combine the universally correct solution (the corresponding energy profile is given by the blue curve) taking either of the solutions correct in the respective limits as first expansion terms. We shall use this possibility later. What we want to study here are the concepts bound to either approximation.

AOs vs. MOs. As we mentioned previously quantum mechanics serves us, but also restricts our phantasy in our (chemists') search for relevant concepts. It is believed that the concepts are somehow better when related to "observables" which are "good quantum numbers": the argotic expressions whose meaning is that the concepts are to be related to an eigenvalue of an Hermitian operator. In such a simple model, the choice is rather limited so we address the *number of electrons* operator. For the HF function eq. (9) we have:

$$\langle \hat{n}_s \rangle = 2$$

thus, the average population of the occupied *symmetric* MO is two, but it is not the entire story: the *dispersion* of this *physical quantity*: $\sqrt{\langle (\hat{n}_s - \langle \hat{n}_s \rangle)^2 \rangle} = 0$; it vanishes, which is equivalent for the HF WF to be an *eigenvector* of the operator of the physical observable "number of electrons in the symmetric MO" which is, thus, a "good quantum number." Due to this, electrons can be ascribed this symmetry label. The concept of MO and its relatives are suitable and valid, for example, one can ascribe a definite energy to an electron occupying this symmetric MO and this makes sense.

But what happens to the MO based concepts in the opposite—infinite separation limit? In this case we again know the exact answer: at the infinite separation the H_2 molecule is in the HL state which can be combined from two Slater determi-

nants with double occupation of symmetric and antisymmetric MOs:

$$\frac{1}{\sqrt{2(1+S^2)}}((1+S)|s_{\downarrow}s_{\uparrow}| - (1-S)|a_{\downarrow}a_{\uparrow}|)$$

$$a(\vec{r}) = \frac{1}{\sqrt{2(1-S)}}(l(\vec{r}) - r(\vec{r}))$$

with $S \rightarrow 0$. In this case the populations of the MO's are almost equal

$$\langle \hat{n}_s \rangle \approx \langle \hat{n}_a \rangle \approx 1$$

But this is still a minor problem; the major one is that

$$\sqrt{\langle (\hat{n}_s - \langle \hat{n}_s \rangle)^2 \rangle} \approx \langle \hat{n}_s \rangle$$

and the same is true for the antisymmetric MO. Numbers of electrons in the MO's are bad quantum numbers; no specific symmetry label can be ascribed to either of electrons (one cannot even say that there is one electron in *a* and another in *s* MO—no way). All concepts based on the MO approximation to the exact WF collapse.

This is not a defect of only the HF function: the same happens to the HL one when applied in a wrong place. In the HL state the average number of electrons on either end is:

$$\langle \hat{n}_l \rangle = \langle \hat{n}_r \rangle = 1.$$

The dispersion:

$$\sqrt{\langle (\hat{n}_l - \langle \hat{n}_l \rangle)^2 \rangle} = \frac{S}{\sqrt{1+S^2}} \ll \langle \hat{n}_l \rangle$$

is small (the same for the right end) provided S is small enough. Only in this case the numbers of electrons on either end are "good quantum numbers" and it makes sense to talk about them—it is a relevant concept. This, however, never happens for the HF picture. The mean values are the same, but they are accumulated equally from the state with a definite number of electrons and the ionic contribution eq. (11) with the same mean value, but collected over two atomic states: one positively (H^+) and another negatively (H^-) charged; dispersions are going to be large:

$$\sqrt{\langle (\hat{n}_l - \langle \hat{n}_l \rangle)^2 \rangle} = \frac{1}{\sqrt{2}} \approx \langle \hat{n}_l \rangle$$

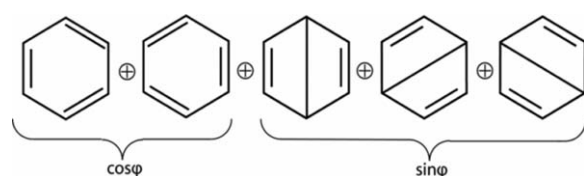
and the concept of an electron residing on an atom (AO) is senseless.^[33] We also recognize here the main defect of using nonorthogonal orbitals for the purpose of developing concepts: they cannot be eigenvectors of any Hermitian operator, thus, whatever physical quantity in such a state has nonvanishing and eventually considerable dispersion. Orthogonal states, by contrast, can be at least in principle selected as eigen

states of some physical quantities. This illustrates a subtle distinction between the concepts introduced (defined) on purely mathematical grounds and those additionally constrained by the requirements imposed by quantum mechanics (physics). The possibility to perform *calculations* in either basis masks the fact that only the orthogonal ones suit for interpretation purposes. In the basis of the symmetric (Löwdin) orthogonalized AOs ($r^{\perp}, l^{\perp}$) the HL state built in the original (nonorthogonal) AO basis has the same form of the general bond *germinal*^[34] with the amplitudes of the homoeopolar and ionic contributions (eqs. (10), (11) with the original nonorthogonal AOs (r, l) replaced by ($r^{\perp}, l^{\perp}$)) uniquely determined by the overlap integral S of the original AOs.^[35] Admixture of the ionic states built upon orthogonal AOs is responsible for the dispersion of the atomic populations in either case.

We see that the question of relevance of various chemical concepts has no universal answer: for different molecular geometries the relevant concepts are also different; those of MO, orbital energy, so forth. are senseless for the distances where the red curve starts going too far away from the blue one. Similarly, it makes no sense to talk about pairing of two electrons residing on two ends of the bond when the beige curve is too far away from the blue one. At the first glance, it goes about the difference between “representations”—the MO or AO ones, but it is not precisely the case. One important detail changes the situation: the descriptions are equivalent irrespective to representation: we can have the exact function starting either from HF (MO-based) or HL (AO-based)—this is mathematical equivalence, but here the physics intervenes: by taking these or those values of the Hamiltonian parameters t and U we *prepare* our two-electron system in that or another state and for differently prepared physical states of the molecule different concepts are valid. It makes no sense to judge differently prepared fish, sushi, and fish-n-chips, following the same criteria.

The same or not the same?. The difference between the MO and VB pictures of the molecular electronic structure has serious consequences. In the above example, we can say that even in the worst cases the correct WF still contributes 50% to the WF of the “wrong” approximation or inversely that the correct WF is at the 50% level contaminated by the wrong one. One could live with this (e.g., by applying the Löwdin partition to the Hamiltonian with the projection on the approximate WF selected on some grounds) unless the situation would not turn worse in more involved cases one of which we consider below in some detail.

The most serious concern was brought to the spin-valence theory by the benzene π -system which, however, gave a hard



Scheme 5.

time yet to Kekulé. One cannot ascribe unique distribution of valence dashes/Lewis pairs, which thus cannot be localized: the situation described as “oscillation” by Kekulé himself and dubbed as “resonance” by Pauling. It was also Rumer who considerably contributed to solving this problem by introducing Rumer diagrams:

—the set of functions (invariant products) with the shown pairing patterns, which are linearly independent and, thus, can be used to uniquely represent whatever singlet *homoeopolar* function—one with single occupation of each site by an electron. The ground state of benzene π -system is one with the amplitudes of the diagrams with the value of φ determined from the energy minimum condition.

We can frequently read something like “as in the benzene π -system the bonds are nonlocalizable and a resonance takes place it is advisable/convenient/reasonable to introduce delocalized description of this system and to construct the WF as a single Slater determinant of the occupied MOs’ as proposed by Hückel.^[36] In this case, as in that of H_2 the MOs can be obtained from the symmetry considerations. The Hückel solution is exact for $U=0$ and remains a HF solution for arbitrary U .^{§§§} A VB reading of a solution similar to the Hückel one (somewhat improved by taking into account electron correlation at a moderate value of interaction) for benzene performed once by hand^[37] yields the squared overlap between the Hückel solution and the entire subspace spanned by the Rumer states (Scheme 5)—the weight of the homoeopolar configurations in it—to be 14.7 percent. That is to say that Pauling and Hückel had suggested two pretty different WFs for the benzene π -system so that the “logical explanation” quoted above makes no sense and “a rivalry between the MO and VB pictures”^[15] is pretty real. Moreover, the fantastic triply (Scheme 6) ionized structures contribute to the above correlation improved Hückel solution by 4.1%.^{¶¶¶} This cannot be a coincidence and it is not—a general theorem yielding the total weight w_k of the k -ionic configurations in the Hückel solution of a cyclic polyene (linear chain of atoms supplied by one π -orbital each with periodic boundary conditions) with $2n$ nodes:

$$w_k \rightarrow \binom{n}{k} 2^{-n}; w_k = w_{n-k},$$

had been proven.^[38] The case of HF function of H_2 is covered by this formula. In the (noncorrelated) Hückel state of benzene the weights of the homoeopolar and triply ionic configurations are both equal to 12.5% (1/8). The most of the weight belongs to singly and doubly ionized configurations (37.5% each, to be compared with, respectively, 48.6 and 32.6%, obtained by the hand-made VB reading^[37]). In *real* benzene (polyene) the k -ionized structures have much smaller weight than in the

^{§§§}We refer here to a Hubbard-like model of benzene: with nearest neighbor one-electron hopping and on-site only electron-electron repulsion.

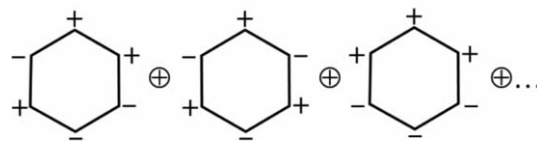
^{¶¶¶}One can read^[4] (if one has a desire, of course) about these structures with all appropriate comments about their inventor and after that, probably, agrees with the present author’s suggestion to extend the known Einstein’s saying “Der Herrgott ist raffiniert, aber boshaft ist Er nicht”—“Subtle is the Lord, but malicious He is not” by further “He has only a great sense of humor”.

noncorrelated/noninteracting case, as they acquire the diagonal energy matrix elements of kU and their contribution is suppressed. The homoeopolar structures contribute much more than fully ionized ones. But to acquire this result one needs to take into account electronic correlation. The situation is very problematic as the entire existing solid state quantum chemistry computer code imposes the Hückel view of the electronic structure of solids (called “tight-binding approximation” in its context) by using the Bloch theorem/sums for representing the electronic structure of a crystal. In the limit $n \rightarrow \infty$ the weight of the homoeopolar structures in the many-electron function derived from the crystal orbitals vanishes ($w_0 \rightarrow 0$). Thus, the available numerical methods have no chance to reproduce the states analogous to the Pauling state in benzene in case they occur in the solid state material. However, the Pauling-like—the nonmagnetic insulating state with delocalized bonds—resonating valence bond (RVB) state was seriously considered as a candidate ground state of high- T_c cuprate superconductors.^[39] A similar state has been successfully applied for explaining the otherwise puzzling physics of CuNCN.^[40] This seems to be an open problem which is incidentally rarely recognized as such.

Diversity of Chemistry. Not only wandering in the configuration space of a single molecule can bring one to the area where his/her habitual concepts break down. It is easy to check that the one-center Coulomb repulsion (U) for the orbitals with principal quantum number n centered on an atom with nuclear charge Z and hopping parameter (t) for a pair of such atoms scale, respectively, as

$$U \sim \frac{Z}{n}; \quad t \sim \exp\left(-\frac{Zr}{n}\right).$$

Obviously, pairs of valence AOs belonging to different values of Z and n may occur in completely different regimes so that the HF suits better for some pairs of AOs and the HL for the others. This prevents any uniform picture of (molecular or solid) electronic structure from being universally valid either for different interatomic separations, or for different compositions coded by nuclear charges Z_x or for both. This situation is perfectly foreseeable for transition metal dimers where, say, $(n+1)s$ - and $(n+1)p$ -orbitals fall in the HF regime whereas nd -orbitals fall in the HL regime. The same applies in the solid state context when it comes to description of transition/rare-earth metals or their compounds where the “bands” stemming from different AOs may occur in different physical regimes as well. The aforementioned “existence theorems” assure the possibility to get a numeric answer by brute force, but do not lead to any qualitative understanding. The lack of an approximation uniformly valid in different parts of the chemical parameter space $\{Z_x, \vec{R}_x\}$ prevents the formation of any common set of *concepts* pertinent to its entirety. This perfectly reflects the experimental situation in chemistry: enormous diversity of behaviors of chemical species leading even to social consequences like appearance of different (sub)communities of organic and inorganic chemists. The realm of the



Scheme 6.

former ones is fairly described by the structure formulae of Schemes 1–3 which are eventually useless when it comes, for example, to open shell d -complexes being the zone of responsibility of the latter. Ironically enough the HF MO LCAO approximation which is currently the starting point of all numerical studies is equally poor for both: it requires considerable efforts to recover the successful and intuitive picture of individual two-center bonds and needs serious correcting terms when it comes to describing the simplest chemical act—a single bond cleavage. Conversely, a material containing transition metal or rare-earth ions electrons populating MOs or bands spanned by $4s$ - and $4p$ -orbitals of a transition metal hybridized with valence orbitals of “light” atoms like oxygen, so forth, fall in the HF regime, whereas d - (and even to a greater extent f -) shells fall in a regime close to the HL one, but aggravated by strong Coulomb interactions and approximate degeneracy of the states in these shells. As a result the electronic WF acquires quite a different structure: neither single Slater determinant of the occupied molecular or crystal orbitals nor an assembly of individual bonds, rather one with fairly isolated d/f -shells preserving features characteristic for the respective free ions turns out to be suitable. This setting formalizes the phenomenology of the crystal field theory that successful in describing transition metal complexes. It produces the relevant concepts, like “strong” and “weak” fields felt by the isolated d -shell, its splitting, local multiplets residing in it, so forth. having no correspondence in “organic” chemistry. More detailed account of the results obtained under this approximation is given in Ref. [41] on the example of iron complexes.

Nomenclature and geography

From the simplest example of H_2 we see that a well or vague definition of the concept of an atom in the molecule depends on the actual physical situation. In a way our conclusion is quite chemical in nature. It is possible to distinguish between a “daltonistic” atom: one with a specific composition that is with a known integer number of electrons and a small dispersion of that number, or a “bertholistic” one with some (already arbitrary) average (in terms of the number of electrons) composition and considerable uncertainty (dispersion) of it. Both can happen, depending on the physical situation predetermined by the point in the $\{Z_x, \vec{R}_x\}$ space and, in principle, the situation does not differ from that described in (W.H.E. Schwarz’s reply to question 2 in Ref. [3]). Physically, atoms do not exist at high temperatures and do exist at lower ones, which justifies application of the corresponding concepts under the relevant external conditions. What, probably,



Figure 23. O.N. Witt (1853, St. Petersburg—1915) the author of the concept of *chromophore*. Photo ca. 1905 by R. Dührkoop (1848–1918) originally published in E. Noetting, Ber. Deut. Chem. Ges., 1916, 49, 1751. (Source: Wikimedia).

confuses “topologically thinking chemists”^[3] is that nuclei always exist in the chemical setting, which makes an impression that a daltonistic atom either has to exist always or is not allowed to exist at all. In fact, there is no dilemma since either atom may exist under appropriate conditions.

The above example shows that the fuzziness of the concept of “an atom in a molecule” is deeply related to the physical situation in each specific system. It is instructive to see how similar considerations apply in a more general setting. Looking at the benzene molecule in equilibrium one easily recognizes that for symmetry reasons the entire (complete) basis of one-electron states can be classified into σ - and π -subspaces orthogonal to each other. Nobody will be surprised by the statement that the number of electrons in the π -subspace equals to six almost exactly ($\langle \hat{n}_\pi \rangle \approx 6$). It is precisely so for the HF treatment of this molecule and whatever thinkable correc-

tions are vanishingly small.^[42] It is also very likely that $\sqrt{\langle (\hat{n}_\pi - \langle \hat{n}_\pi \rangle)^2 \rangle} \approx 0$. Thus, we identified a “daltonistic” object not bound to any specific atom (nucleus), rather to a subspace of one-electronic states. This object can be considered as an observable one not only formally—as an eigenvalue of the respective Hermitian operator—, but also in an operational sense, as it can be characterized spectrally. On the same grounds as in benzene one can identify π -subsystems of a specific composition ($\langle \hat{n}_\pi \rangle$ —almost integer; $\sqrt{\langle (\hat{n}_\pi - \langle \hat{n}_\pi \rangle)^2 \rangle} \approx 0$) in other *planar* molecules as well observable spectrally. This sets the situation in the direct relation with the old fashioned, but very useful concept of *chromophore*^[43] giving to a molecule its *color* as proposed by the personage of Figure 23. We can consider an arbitrary set of orthogonal subspaces giving the complete space of those as a direct sum and check whether they satisfy “daltonistic” condition ($\langle \hat{n}_A \rangle$ —almost integer; $\sqrt{\langle (\hat{n}_A - \langle \hat{n}_A \rangle)^2 \rangle} \approx 0$) so that the physical quantities $\langle \hat{n}_A \rangle$ are “good quantum numbers” and, thus, the many-electron state over which the averaging $\langle \dots \rangle$ is assumed is at least approximately an eigenstate for the system of operators $\hat{n}_A$. The approximate WFs making these relations exact are nothing, but the group functions^[44] which sets the basis for the new concept of semiempirism in quantum chemistry.^[45] Namely, one has to choose the form of the trial WFs on the basis of the observable entities: generalized chromophores and to compensate the deficiency of this approximate form of WF by the Löwdin partition.^[46] It is of interest to recognize that the WF of the old spin-valence theory belongs to this class since it is an antisymmetrized product of the HL functions describing *individual* isolated bonds built in orthogonal *carrier* subspaces. The distribution of individual bonds (as well as known cases when a unique distribution is not available) is coded by the *iconic* structure formulae filling the organic chemistry books and papers. With a very reasonable allowance one can say that the IUPAC nomenclature of “organic” compounds is designed to call both the electron-nuclear Hamiltonian (characterized by the composition $\{Z_d\}$) and the electronic WF by a *single name*.^[47] By contrast, looking at a book on inorganic optical spectroscopy^[48] one immediately recognizes that compounds there are not represented by structure formulae rather classified according to the number of electrons in their d-shells. Taking this compendium of experimental data as a generalized *observation* we conclude that the d-shells of the transition metal complexes represent another example of observable entities characteristic, namely, for this class of molecules. The fact that d-orbitals are not well defined is immaterial here: the spectra are observable and interpretable precisely for that or another *integer* number of electrons. The idea of building the notation (coordination) for molecules upon their electronic structure in terms of groups of more general form than the two-center two-electron bonds and conjugated π -systems usual for organic chemistry, had been discussed recently.^[49] The general scheme proposed there is very attractive, however, it misses the physical/experimental grounds for selection and assignment of electrons to

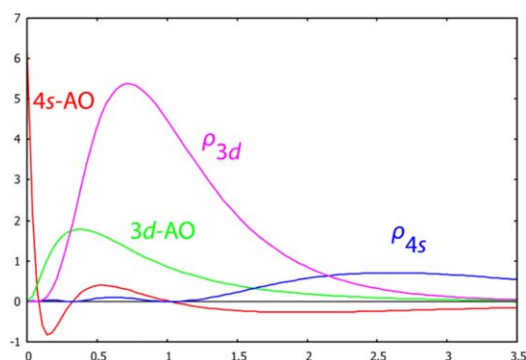


Figure 24. Radial parts of the 4s- and 3d-AOs (red and green, respectively) of the Fe atom,^[53] and the corresponding electronic densities (blue and magenta, respectively) calculated from them assuming the population of the d-shell with six and of the s-shell with two electrons.

the groups. Combining it with *observable chromophores* and/or combinatorial optimization (see below) with respect to various segmentation of the total one-electron space and to distribution of electrons among these subspaces can tentatively produce a unified picture embracing uniformly the physical, substantial chemical, and formal nomenclature aspects.

Having already three (or four) examples of observable (daltonistic) intramolecular entities: d- (or f-) shells, π -systems, atomic cores, and, eventually two-center, two-electron bonds we can readdress the old problem of identifying fragments within a molecule, that is its “geography.” The story goes back to Ruedenberg who gave a very nice discussion in the second and third paragraphs of p. 327.^[50] The quotation is too long to be given here, thus, the reader is urged to have a look in the original article and see how the discussion of fragmenting oscillates between fragmenting molecular energy and that of molecule itself. Ruedenberg stresses the importance of each “observable” fragment of energy referring to a molecular fragment provided the energy fragment can be fitted to a reasonable curve, but the entire discussion equally (if not better) suits for justification of observability of molecular fragments themselves—that is, to defining observable “geographical regions” within the molecule. Literature reports attempts of defining intramolecular regions in the direct space,^[51] but using even “the best known observables of all times and nations,” those of the QTAIM, does not help as the dispersion of the electron population of atomic basins in the H_2 molecule is as large as that of the AO's in the HF solution^[52] (if the HF approximation is used for the calculation) that is the latter *entity* in this sense is not less (but not more) observable, than the QTAIM basins. One should not be surprised: building walls in the $\mathbb{R}^3$ space for a quantum particle—an electron—is an attempt to localize it, but the uncertainty principle makes its momentum uncertain; the direct space localization is going to change in the very next moment. Imagine that you get a good kicking every time you decide to find out where you are. It is, precisely, the destiny of an electron.

A simple atomic physics example shows us that segmentation in the quantum world indeed follows the border lines drawn in the Hilbert rather in the direct space. The AOs of two (valence) shells of the iron atom as depicted in Figure 24 are nonvanishing for the same range of the distances. Although the density maxima are visibly shifted relative to each other, the distance ranges where electrons of different shells reside significantly overlap. These are the nodes of the AOs which guarantee the orthogonality of the s- and d-functions and by this assure the segmentation—in fact—the quantization of the $\mathbb{R}^3$ space. One also easily singles out the cores, and in this case it is again the extra node which makes the valence 4s-AO be orthogonal to the core 3s-AO. Namely, the orthogonality of WFs is the true border in quantum setting, but it runs in the Hilbert space. So defined “regions” with the well-defined composition represents precisely what was required: the *observable* parts of a molecule and, thus, represent its true geography. Belong they to different areas in the direct space (like cores of different atoms)—good for them, but it is not mandatory. We have to

learn from Mayer who says that he orients himself much better in the Hilbert space than in $\mathbb{R}^3$.

His name is bond. . .

The idea of chemical bonds can be traced back more than 2000 years. These ideas are pretty much intuitive, in a way, first which comes to a human's mind. By contrast, the concepts, shaping our contemporary understanding of molecular and crystalline electronic structure seemed to be very unusual at a first glance. Instead of local bonds which had been accepted (even their resonance which anyway explained one incomprehensible—oscillation—by another incomprehensible—resonance) due to efficiency in describing the entire world of organic chemistry, a completely new picture of delocalized MO's arose. These concepts were in a deep contradiction with already established and fundamentally correct “local realistic” view of chemistry. The MO based concepts are frequently portrayed as inherently ‘quantum’ and as such counter-positioned to allegedly “classical” picture of local bonds. Obviously, ascribing quantum character exclusively to the delocalized MO-based picture is wrong, as even the isolated local bonds as they appear in the theory of spin-valence are inherently quantum. Despite that at a certain moment it became a widespread viewpoint to deny “quantum” reality of chemical bonds at all. The characteristic quotation^[54] reads: “The concept of bond appeared little by little in the mind of chemists from empirical observations. From the wave-mechanical viewpoint it is not an observable. Therefore there is no precise operator associated with that concept.” The real source of problem is that the MO approximation turned out to be a dominating if not unique one in the realm of molecular science so that the related concepts turned out to be imposed by force.

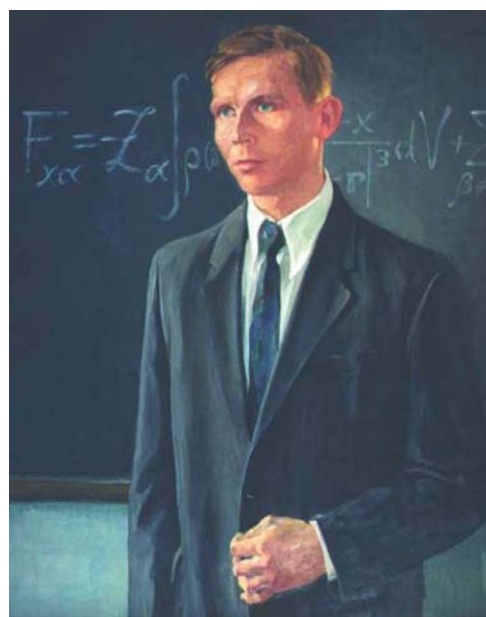


Figure 25. H. Hellmann (1903, Wilhelmshafen—1938, Moscow) the author of the first monograph entitled “Quantum Chemistry.”^[60] Photo shot by W.H.E. Schwarz (1999, Siegen) from portrait painted by T. Livschitz after permission of T. Livschitz and Deutsche Busen-gesellschaft für Physikalische Chemie, published thanks the kind permission of Prof. Dr. W.H.E. Schwarz.

These concepts are 100% pertinent to the MO based picture of the molecular (crystalline) electronic structure and have no meaning beyond it. The local bonds do not exist in the MO approximation, although the number of various proposed “bonding indices” counts by dozens. They are fairly able to produce some numbers, but neither of them is able to answer a simple question: “what is chemical bond.” A recent controversy^[55] around C_2 highlights this unsatisfactory situation.

The uncertainty with the definition of chemical bond can hardly be tolerated: it goes about the own (discrete) topology of chemistry: bound or not bound. The definition coming from the position of authority reads: “There is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient *stability* to make it convenient for the chemist to consider it as an independent molecular species.”^[56] The good portion of criticism in respect of this definition bases on involvement of “the chemist” with his/her “convenience.” The authors^[51b] assume that the above quotation refers to “an ideal chemist.” However, the text refers namely to “the chemist” most probably a good acquaintance of the responsible editors. This too personal reference had been excluded from the renewed definition.^[57] “When forces acting between two atoms or groups of atoms lead to the formation of a *stable* independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. Not only directed covalent bonds characteristic of organic compounds, but also bonds such as those existing between sodium cations and chloride anions in a crystal of sodium chloride or the bonds binding aluminium to six molecules of water in its environment, and even weak bonds that link two molecules of O_2 into O_4 , are to be attributed to chemical bonds.” We see that within *ca.* 15 years the definition of a concept fundamental for chemistry has significantly changed. The only survived component is the reference for “stability” which is purely quantitative characteristic eventually leading to a vicious circle when applied to *derivative* concepts. For example: “Chemosorption: Adsorption which results from *chemical bond formation* (strong interaction) between the adsorbent and the adsorbate in a monolayer on the surface.” Conversely: “Physisorption: Adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved.” The references to the intimate mechanisms (either interrelation between kinetic and potential energy or significant change in electronic orbital (!) patterns) contradicts to the view of chemistry as of “purely empirical science.”^[58] The reference to a completely unknown O_4 additionally confuses the situation: who knows what is the mechanism of bonding in it, if the fact of this bonding (stability) had not been well established yet?^[59] The story reflects a rather prob-

lematic situation with the most fundamental concept of chemistry.

The only possibility of sequential analysis is due to the *theorem* by the personage of Figure 25. Its formulation (partially shown on the background of that Figure):

$$F_{xx} = -Z_\alpha \int \frac{\rho(\{\vec{R}_\alpha\}|\vec{r})(X_\alpha - x)}{|\vec{R}_\alpha - \vec{r}|^3} dV + \sum_{\beta \neq \alpha}^A \frac{Z_\alpha Z_\beta (X_\alpha - X_\beta)}{|\vec{R}_\alpha - \vec{R}_\beta|^3} \quad (13)$$

expresses the x-component of the force acting on the α th nucleus in a molecule through the integral of the one-electron density $\rho(\{\vec{R}_\alpha\}|\vec{r})$ —depending on the nuclear coordinates and their charges as on parameters—(first term) and the charges of all other nuclei (second term). This expression clearly demonstrates that the only reason for a molecule to be a single (bound/stable) entity is provided by the attraction between nuclei and electrons, since the nuclei and electrons separately always repel each other. The bonding *energy* cannot be anything else as the integral of the force with components given by eq. (13) along the path bringing the nuclei from the infinity to the current configuration. Its totally classical appearance is, however, deceptive as the density must be calculated quantum mechanically. The fact that electrons are not localized in points yet does not make them quantum objects. Performing the calculation with *classical* approximation to the electronic density in H_2 in that sense that electrons are assumed to obey the Kolmogorov statistics:

$$\rho_K(\vec{r}) = l^2(\vec{r}) + r^2(\vec{r}). \quad (14)$$

yields a very shallow minimum (even shallower than that on the beige curve).^[61] It is yet a happy coincidence, as the classical treatment is implemented in eq. (14) only partially: the atomic electronic densities are allowed to follow the new positions of the nuclei, but nothing more. Had the arbitrary adjustment of the density been allowed, the Earnshaw theorem^[62] would immediately lead to collapse, so that no minimum would appear at all. The bonding (like any kind of stability of electron-nuclear system) is exclusively quantum phenomenon. Although it may sound somehow extravagant to reiterate the quantum character of bonding about 90 years after it had been unequivocally established, an impatient reader has to realize that the entire X-ray diffraction community uses the *classical* densities similar to eq. (14) to fit their data^[63] and calls the result of this fitting “experimental density.” This way of doing things is *built in* into software processing the X-ray raw data so that the overwhelming majority of its users do not know what is in. Thus a reminder is, hopefully, not futile.

What do the bond measures measure?. Deriving densities for two “quantum” solutions considered so far:

$$\rho_{HL}(\vec{r}) = \frac{1}{1+S^2} (l^2(\vec{r}) + r^2(\vec{r}) + 2SI(\vec{r})r(\vec{r}))$$

$$\rho_{\text{HF}}(\vec{r}) = \frac{1}{1+S} (\rho^2(\vec{r}) + r^2(\vec{r}) + 2I(\vec{r})r(\vec{r}))$$

we see that both contain the cross (interference) term—the product of the AOs which remarkably complements the classical density in the internuclear region.^[64] This quantum excess contributes to the force acting on the nuclei. The HL function underestimates this term by the factor $S(1+S)/(1+S^2) < 1$ as compared to the HF one. This explains the relative shallowness of the HL minimum on the H_2 energy profile (beige) as compared with the HF (red) and exact (blue) value. The multiplier scaling the interference term (also known as “differential overlap”) is a reasonable indicator of namely the “quantum” contribution to the density augmenting the bonding. In a many-atomic setting several MOs contribute to this factor:

$$\rho(\vec{r}) = \sum_{i\mu\nu} f_i c_{i\mu} c_{i\nu} \varphi_\mu(\vec{r}) \varphi_\nu(\vec{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\vec{r}) \varphi_\nu(\vec{r}) \quad (15)$$

(summation over i 's runs over the natural MOs—in case of the HF treatment these may be occupied canonical MOs—eigenvalues of the Fock operator; f_i 's are the occupation numbers—eigenvalues of the electron density operator) where either left or right hand sides as well as multipliers and terms on the right hand side are $\{\vec{R}_\alpha\}$ dependent. We see that the Coulson bond order $P_{\mu\nu}$ —the off-diagonal element of the one-electron density matrix between the involved AOs—enters in the expression for the force eq. (13) and can be used in deriving general statements, like bond order/bond length relation.^[65] That is to say that after having appeared on the left hand side of its definition:

$$P_{\mu\nu} = \sum_{i\mu\nu} f_i c_{i\mu} c_{i\nu}$$

it reappears on the right hand sides in expressions for different physical quantities. It seems to be excessive to sum the Coulson orders referring to different pairs of orbitals $\mu\nu$ centered on different atoms, as it basically is nothing but summing apples with oranges. The real bonding effect for each such pair is stipulated by the properties of the product $\varphi_\mu(\vec{r})\varphi_\nu(\vec{r})$ (in fact, by the component of the electrostatic field induced by this density). The simplest to trace is the sign of this product (in the internuclear region), but even for the equal signs the effect of each pair is individual, unless some special conditions apply. This diversity is, probably, the source of uncertainties in conclusions^[55] about the number of bonds in C_2 based on similar summation.

If the nonorthogonal AOs are used, a close relative of the Coulson bond order—the Mulliken overlap population—is usually defined. The interference contributions to the density in this case are integrated and produce the overlap integrals serving as weights at the contributions to the Coulson bond order. These components sum up to the total number of electrons. The problems of phase relations between AOs $\mu\nu$, that is, of the sign of the product $\varphi_\mu(\vec{r})\varphi_\nu(\vec{r})$ are solved by this, but not that of distinguishing individual contributions of each such pair. In the solid state context a similar tool (with energy

resolution) is known under the name of the crystal orbital overlap population.^[66] Either produce a potentially useful numerical indicator, but one has to be sure that in contrast with the Coulson bond order these indicators do not enter to any kind of expression for energy or force (or whatsoever other physical quantity)—namely, the differential overlap itself is the important quantity, not its integral; the latter may be even vanishing—if the orthogonal AOs are used—but they equally well reproduce the sought quantum effect. Continuing in the same spirit one can address the electron-nuclear attraction operator. Then the overlap integral in the sum for the overlap population gets replaced by the matrix element of the attraction operator between the AOs:

$$-\sum_\alpha \int \frac{Z_\alpha \rho(\vec{r})}{|\vec{R}_\alpha - \vec{r}|} d^3\vec{r} = \sum_{\mu\nu} P_{\mu\nu} V_{\mu\nu}. \quad (16)$$

By this the entire attraction energy present in the system is exactly expressed through the Coulson bond orders, which are, thus, physically substantiated descriptors of bonding. The sign of each term on the right hand side unequivocally classifies the interaction between the involved AO's as bonding or antibonding not “in general,” but *for each given pair of AOs*. The same classification applies to the individual MOs contributing to the Coulson bond orders. It is advisable to use these criteria when deciding whether an MO is bonding or not rather to rely upon that or another “looking out.”^[55] In the solid state context the energy resolved descendant of eq. (16) is known as the crystal orbital hamilton population.^[67]

The above quantities can be qualified as “direct bonding measures” as they address precisely the quantum mechanical contribution to the bonding: the density excess emerging from the “constructive interference” of two waves (orbitals). They are easy targets for criticism due to involvement of AO's in their definitions. However, the analysis in terms of atoms and their attributes is relevant in the chemical setting. Chemists build their molecules of atoms not of nuclei and electrons, even less of electrons, nucleons and mesons, and so forth. When talking about chemistry it is precisely what we want to know: how some combination of *atoms* is positioned on the energy scale relative to the same collection of atoms put in the infinity.^{****} Let us reiterate once again: the *concept* of the Coulson bond order and its relatives appear due to some approximation involved in the consideration—namely, AOs are

****The atom concept can be formalized (if one needs a formal definition) in terms of strong correlation between positions of a nucleus with some Z_α and the same number of electrons. The AOs represent the character of this correlation with that or another degree of precision. Those who are unhappy with an involvement of an unobservable object (AO) in the theory are free to repeat the derivation for the H atom in terms of observables: either density *matrices* or Green's functions (propagators), and may be sure that if the result is different from one written in a textbook in terms of AOs, they have made a mistake (the resulting density matrix must be the operator projecting to the known AOs). The reference to the density *matrix* and not to the density is not accidental. Using the density—that is the diagonal of the density matrix is not enough: in the diagonal the phase relations between different points in space get lost. Neither the two-slit experiment can be described in terms of the density only, nor the kinetic energy can be calculated.

used to represent the density. But it is an advantage, not a drawback. In the simple case of H_2^+ one can obtain the exact solution^[68] not involving any AOs, derive density from it and it will be the exact one. But this exact knowledge brings us nowhere.^{†††} The exact solution is available for this only case and provides no tools (concepts) for discussing more involved ones. The Mulliken quotation "...the more accurate the calculations became the more the concepts tended to vanish into thin air. So we have to ask, should we try to keep these concepts – do they still have a place – or should they be relegated to chemical history."^[69] is normally considered as an urge to reduce the number of concepts. This quotation goes in a line with 'a half' of the Fock statement.^[32] However, the situation in our science is opposite: when everything is calculated exactly we are left with numbers only (which we actually need not that much) and sacrifice for them all the tools which could be used for our orientation in a wider area where the calculation is not available. The other direction of the Fock reasoning^[32] applies. We need concepts: the complexes of variables independent in the "exact" setting, but turning out to be correlated or even dependent in a specific class of situations, which allows (due to dependence) to replace (may be, different complexes for different situations) these complexes by a single collective variable. That is what Coulson meant by "understanding." Identifying such situations and relevant complexes of variables is the real content of any informative theory.

The differential overlap of the original AOs (those of the free atoms) does not exhaust all possible contributions to the density variation along the path from the infinite separation to the actual geometry. Other contributions (the contraction, penetration, polarization, and electron transfer) in details analyzed yet at a pretty early stage^[50] may be considered as a basis of classification of bonding interactions provided some theorems are formulated and proven about these contributions, which eventually allow one to identify them experimentally. Conversely, it is worth saying that despite repeatedly stressing the importance of the differential overlap for bonding, the energy contributions^[50] are pretty counterintuitive and do not unequivocally support the idea of its importance. In fact four contributions of opposite signs and of similar absolute values contribute to the result^[50] (Table in paragraph 2 of chapter 7) and it is not possible to say that one simply compensates another and some other produces the final result. Moreover, the main *negative* (energy lowering) contributions are the *attraction to nuclei* under the orbital contraction—one-center terms—intuitively having nothing to do with the bonding—and the *kinetic energy reduction* due to interference (differential overlap). We suspect that this inconsistency arises because of usage of nonorthogonal AOs for analysis. Had the orthogonal AOs been used, the destabilizing effect of contraction upon the kinetic energy would not be so large and thus its reduction will not be necessary. The advantages of the orthogonal basis have been outlined above. Their dependence on the geometry does not represent any problem

from our point of view, since as we know since years^[70] the AOs modify themselves throughout the formation of a molecule from atoms (that is the contraction of AOs mentioned above). Thus, the very fact of modification does not represent anything new. Complementing contraction with orthogonalization does not introduce any fundamental difference. We shall explore this possibility at a further occasion.

Do they really want to pair?

The one-electron density itself does not provide/contain enough information to single out its components justifying differentiation of the bonding mechanisms. Although one can notice that the density in some internuclear region is better described by the Coulson bond order $P=2S(1+S^2)^{-1/2}$ with some small value of S (HL regime) than by $P=1$ (HF regime) and on this basis argue that in the former case the bond is rather the antiferromagnetic coupling of the spins of local electrons whereas in the latter case it is a covalent bond, whatever true classification is only possible on the basis of some other observables. In a general formulation the required observables are the reduced density matrices of the k th order (k -RDM's) which derive from

$$\rho^{(N)}(\{x_i\}; \{x'_i\}) = \Psi^*(\{x_i\})\Psi(\{x'_i\}) \quad (17)$$

—the N -electron density matrix (in the coordinate representation) associated with the N -electron WF $\Psi(\{x_i\})$. The density matrix $\rho^{(N)}$ *is an observable* and produces a description equivalent to the WF one. This description for the time being may seem superfluous: it contains information about all many-

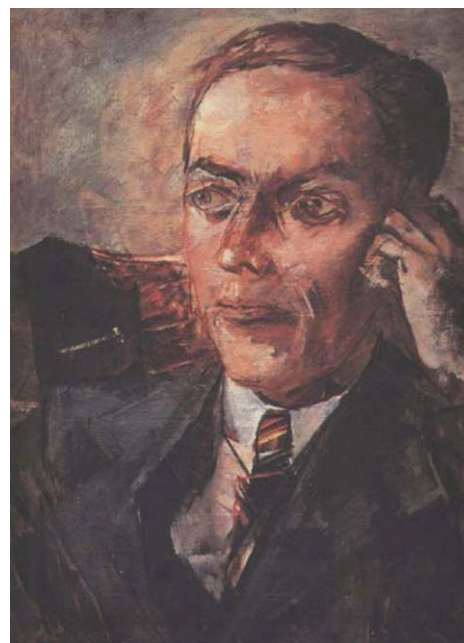


Figure 26. L.V. Kantorovich (1912–1986). Nobel Prize in Economics of 1975 together with T. Koopmans known to the readers of the present issue for the Koopmans' theorem. So it is not surprising that the result of his coawardee can be made useful for chemistry. Portrait (1938) by K.S. Petrov-Vodkin (1878–1939). (Source: Wikimedia).

^{†††}Of course it is useful for checking the quality of approximations and brings an aesthetic enjoyment by itself. But not more and not less.



Figure 27. V.M. Tatevskii (1914–1999) (Thanks to the kind permission of the photoarchive of Laboratory of Molecular Spectroscopy of the Chemistry Department of the MSU).

particle correlations although the experimental techniques which would be able to detect them are not yet developed. The k -RDM's derive from $\rho^{(N)}$ by setting equal last $N - k$ x_i 's and x_i' 's in eq. (17) and integrating over them. This process leads to information loss so that equal k -RDM's of a smaller k 's may belong to different many-electron states with different k -RDM's of larger k 's. The correlations distinguish different many-electron states potentially having the same density. The correlations containing the information about the detailed structure of the WF, like the weights of ionic configurations, are consequently getting lost in the process of reduction producing the k -RDM's. The same applies to spin-correlators and other similar quantities. The simplest of nontrivial k -RDM's, the 2-RDM, is at least indirectly observable already today since it enters in the expression for the energy where it is responsible for the electron-electron repulsion. Also the observable squares of one-electron operators: S^2 , L^2 of the electronic state under consideration express through the 2-RDM. Moreover, a theorem^[71] due to Mazziotti states that **provided** a pure many-electronic state is fully characterized by 2-electronic operators it is equally fully characterized by its 2-RDM. Even this information gets lost in the one-electron density which manifests in theorems, stating that that latter does not depend on the permutation symmetry of the WF, and thus on its total spin^[29] which ultimately leads to known "unfriendliness of DFT to multiplet states".^[72] Eventually these correlations are able to justify the break-down of the one-electron density into components. For example, an accumulation of the density due to population of excited states of the interacting species allows one to qualify the resulting attraction as London (dispersion) contribution to van der Waals interaction.^[73] This program seems to be better physically substantiated than the known

attempts to base the required classification on the point properties of densities and their derivatives (see numerous references in Ref. [3]).

Remarkably, the indirect bonding measures/indicators represent a different group of approaches to the bonding analysis^[74] that explore the way of using the higher RDM's since they concentrate in that or another way on measuring the amount of pairing in the system and on its spatial distribution. The simplest bonding indicator of this type is the Wiberg Index stemming as shown^[74b–g] from the exchange contribution to the 2-RDM: $-P_{\mu\nu}^2$. This form of the indicator solves (like the Mulliken overlap population) the problem of the different phases of $P_{\mu\nu}$ for different pairs of AOs. Nevertheless, the relation between this indicator and energy is misleading: the exchange energy term reduces the total energy (observe the "minus" sign above), but it is not an independent energy contribution, it only modifies the electron-electron repulsion, but does not have any relation to bonding. The same applies to correlation energy: it effectively reduces repulsion, but the bonding reduces as well due to population of the antibonding orbital (it is obvious for the case of H_2) and corresponding reduction of the bond order and, thus, of the interference density.

An interrelation between pairing and bonding is a perpetual topic as Lewis himself. According to Mulliken, who gave an early review of the field,^[64] the idea of electron pairing was very dear to Lewis.^[51b] It has widespread pedagogical consequences: the freshmen chemistry students come to the universities with a firm conviction that "electrons want to pair" and most of chemists even retire with it. Setting aside technical details, the statement that an invariant hides behind each structure formula translates into modern language so that the total electronic spin of a "stable" molecule (one where the forces of chemical affinity come to some equilibrium) equals to zero.^{****} This statement is apparently wrong in general—the paramagnetic (triplet) dioxygen molecule being the best known counterexample. It is thus interesting to trace backwards possible origins of this misconception. Apparently, it goes back to Sylvester, but he only assumed that the structure chemistry formulae represent invariants—not anything else. Gordan and Alexejff inverted the statement and postulated that namely the *invariants* must have some (at least *metastable*) chemical counterparts. But, this idea is a consequence of a tacit assumption of a molecule being a small sphere. In their time Debye had not shown yet that a molecule can bear a permanent dipole moment (1913) and, thus, is not necessarily spherical (not talking about results of L. Pasteur, H. van t'Hoff, A. LeBel, which were completely out of their focus). Although it is not directly related to the spin the very idea of the sphericity is falsified by this. It is amazing that the personages of Figure 19 did not notice that their construct with spin-paired electrons can have only a limited validity: they for sure were

****More general version of this statement is that any energy minimum corresponds to a symmetric state; the counterexample is obvious: the Hund's rule for atoms, which might be opposed by Alexejff who could say that free atoms are not in equilibrium and would be right.

aware about the Hund's rule which states precisely the opposite. This turned by now a huge infernal machine under the VB theory: the entire realm of open-shell transition metal complexes had been set aside by this deliberate assumption. The variety of the WF types being considered in theoretical chemistry turned out to be drastically restricted by this.

It is, thus, of interest to understand the reasons why the pairing is so ubiquitous, and two-electron bonds that wide spread in the chemistry realm. Our hypothesis is that the paired functions (products of invariants) are for some external reason the solutions of the many-electron problem incidentally giving birth to various additive schemes. Exploring this hypothesis requires an excursion into a realm of quite refined mathematics which we perform in a "sparing regime." Our previous discussion revolved around the WF description of molecular electronic structure. In the end we, however, arrived to the conclusion that the most interesting issue—the bonding has no other source except the one-electron density—a much simpler object than the many-electron WF. Other famous existence theorems (Hohenberg–Kohn and Kohn–Sham) establish a one-to-one correspondence between the point in the chemical space $\{Z_x, \vec{R}_x\}$, coding the external potential for the electron system, and the one-electron density. This leads to the DFT as an alternative to the WF based approach to the molecular (crystal) electronic structure. A somewhat less ambitious program is to replace the WF not by the one-electron density, but by 2-RDMs which is the highest k -RDM necessary to calculate the total energy.^[75] At a first glance the idea promises great advantages, since the two-electron density needed to calculate the energy is the function of two spatial coordinates only. The 2-RDM is a more involved object—a function of four points in the one-electron coordinate-spin space of x 's, which is any way a big saving as compared to N such points being arguments of the WF. The complexity of the WF translates in that of the N -representability problem since we have to be sure that the function of four coordinate-spins is indeed derived by the multiplications and subsequent integrations from an N -electron WF. That latter is antisymmetric with respect to transpositions of each pair of its arguments and has to correspond to a definite value of the total spin (for the non-relativistic Hamiltonian independent on spin variables). These requirements can be reformulated as a system of *linear* inequalities.^[76] The N -representability problem for 2-RDMs turned out to be immensely complicated. Until today we know relatively little about the geometry of the set of N -representable 2-RDMs. Two important known are the following: first, the set of N -representable 2-RDM for any N is convex. This means that each 2-RDM can be represented as a linear combination of some 2-RDM's laying on the boundary of this set and even more—in its extreme points. The simplest illustration of this statement is that whatever point of a convex polygon or polyhedron can be represented as a linear combination of their extreme points—vertices. The second statement^[76] is that the 2-RDMs derived from a WF of special form, namely, the antisymmetric geminal power (AGP) are extreme points of the set of 2-RDM's. Much hope has been placed on this result as it turned out that RVB functions are close relatives of the

AGP. There are arguments which allow us to think, that the WFs of the APSLG form^[77]—those representing the electronic structure of a molecule as an antisymmetric product of individual two-electron two-center bonds can be presented as an AGP's as well. Thus, the corresponding 2-RDMs are as well extreme points. This result can be combined with that by the personage of Figure 26 which states that the extrema (maxima or minima) of a linear functional defined on a convex domain are the extreme points of the domain itself (a linear functional defined on a polygon or polyhedron has extrema in their vertices). The construction finalizes by recognizing that the electronic energy is a *linear* functional of 2-RDM.^[75] By this we see that it is possible that at least some of the extreme points corresponding to the AGP/APSLG WFs may be solutions of the electronic problem. This singles out and in way defines purely mathematically the area of "organic" chemistry: that of the 2-RDMs derivable from AGPs. It explains the success and efficiency of the description of molecular electronic structure in terms of localized bonds. For the electronic WFs/2-RDMs of that type the energy acquires an additive form giving foundation to all additive thermodynamic models of unprecedented precision (The original works by V. M. Tatevskii et al. appeared 10 years before)^[78] developed by the personage of Figure 27 or approximate methods of structure optimization known as molecular mechanics (force field). At the same time the AGP's do not exhaust the entire set of the extreme points, otherwise life would be too dull. There are further extreme points of the set of N -representable 2-RDM's which do not have the AGP and thus the isolated bonds form.^[79] Describing the situation qualitatively we can say that the true polygon (polyhedron) containing all N -representable 2-RDMs is only a part of that defined by the AGP vertices, but shares some of its vertices with that former. Wandering in the $\{Z_x, \vec{R}_x\}$ space changes the linear functional defined on the convex domain of the 2-RDM's so that the solutions of the energy minimum problems corresponding to different $\{Z_x, \vec{R}_x\}$ points switch from one extreme point (vertex) to another which tentatively corresponds to a discrete change from one structure formula to another or eventually transforming to a vertex of a completely different type. We postpone the discussion of these issues for further occasions.

Conclusions

Despite enormous progress of computational methods as applied to chemistry the conceptual side of this development seems to remain in some negligence. This contradiction is common to all mathematical theories: one of the most ingenious mathematicians of 20-th century noticed that "object of a mathematical theory is to reduce computations in individual problems."^[80] Also Lejeune-Dirichlet as transmitted to us by Bourbaki^[81] calls us "to substitute ideas for calculations." This vision of what is needed represents an alternative to the urge to graduate students "you have a program ... use it"^[55] in a hope that these latter are in a possession of some more relevant tools than merely a program.

Mathematics alone does not suffice for developing the required ideas. Crucial ingredient is the *physical* theory developing the approximations appropriate either for the entire realm of chemistry (formally described as physics of many-electron systems in strong nonuniform even singular electrostatic fields) or for specific areas of the chemical ($\{Z_x, \vec{R}_x\}$) space by this justifying emerging mathematical structures and explaining their *raison d'être*. Otherwise no matter how refined mathematical models turn out to be completely arbitrary. Historically we see that a physical theory is not necessarily synchronized with mathematical one: its appearance does not mandatory precede the formation of the informative mathematical structure. By contrast, a successful mathematical model may suggest that the required physical theory can be developed (a characteristic example is provided by applications of graph theories in chemistry). The examples informally discussed above hopefully give an impression of how informative theories in the area of chemistry could be developed.

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