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Invited Review

Historical Aspects of the Chemical Bond. Chemical Relationality *versus* Physical Objectivity

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Summary. Chemists have always defined the properties of materials on the basis of the changes observed when they reacted with other substances. Whereas this approach led chemists to relational concepts such as "affinity", "acid", and "oxidant", physicists made measurements of objects they considered unchanged, determining their mass, charge, dipole moment, *etc*. In the middle of the 18th century, the Jesuit *Josip Ruder Bošcović* started thinking about the way in which atoms might be present in crystals, introducing a new concept according to which atoms in condensed phases represented punctual centres of attracting and repelling forces. *Josef Loschmidt* became aware of these ideas through the philosopher *J. F. Herbart*, and it is to *Loschmidt* that we owe the first representation of bonds as atomic spheres penetrating one another. The term "quantum chemistry" was first used by the physicist *Arthur Erich Haas*, who was born in Brno. However, *Hans Hellmann* (1903–1938) was the true founder of quantum chemistry. *Hellmann*, who was shot in Moscow in 1938, was the first person to realize the quantum-physical effect that leads to the chemical bond. In the 1960s *K. Ruedenberg* and others took theory a stage further when – thanks to the concept of the localized electron pair – they realized that the different approaches to the phenomenon of the chemical bond taken by chemists and physicists were largely comparable. This made it possible to bring the differing standpoints largely into line with one another.

Keywords. Affinity; Chemical bond; Quantum chemistry.

Introduction

For centuries physicists believed that they could acquire knowledge *via* isolated objects (rolling balls, planets, elementary magnets, *etc*.). Of course it is possible to use classical mechanics to allocate mass to a body without having to carry out

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thousands of readings in various surroundings and under the most differing circumstances. However, this belief was shattered by the theory of relativity, according to which even measurements of length are dependent on the relative speed of the "object" towards the observer system. The quantum theory exploded the naïve view completely.

In chemistry the situation had always been different. For instance, when it was a matter of determining the content of gold, silver, or copper in an ore, the sample not only had to be broken down and heated, but various reagents (acids, salts, sulphur, mercury) had different effects at different temperatures. This resulted in a variety of reactions: gases were emitted, changes in colour occurred, reguli were formed. It never occurred to anybody that a chemical analysis could contain an undisturbed object. Chemical properties are only manifested in the course of an interaction.

Even Paracelsus pointed out that it is not really possible to divide substances into poisonous and non-poisonous. It depends on the circumstances, on the dose, on a previous habituation effect, on antidotes that are present at the same time, possible stress conditions, and so on. It could now be asserted that in the case of the toxic effect on organisms it is a question of the interaction with an extremely complex system. However, it becomes apparent that the same phenomenon also occurs in the case of the most simple chemical concepts of classification. If the budding chemist finally becomes used to referring to substance A – let's say for instance hydrogen peroxide – as a strong oxidising agent, he then has to discover that this reagent, as soon as it comes together with an even "stronger" oxidising agent B (this can be a potassium permanganate solution) itself becomes oxidised. The most varied species are released on one another in order to gain new information and according to the reaction partner the information to be gained is different. Water reacts with gaseous hydrogen chloride in the sense of a *Brønsted*-base, with ammonia as an acid. Our old familiar water is therefore both an acid and a base! The chemical properties are relational [1]; they determine a bond not to themselves but by taking consideration of their surroundings [2]. *Walter Hückel* expresses this as follows: "Chemical properties are not founded in one substance alone but demand a reaction partner". Chemical properties are therefore reaction possibilities. The Russian chemist *I. J. Bykov* commented aptly, "The chemical properties of a substance are the seeds of its destruction" [3]. The relational character of chemical concepts is what distinguishes chemistry from physics as a discipline operating in a clearly different manner.

On the basis of the history of the central chemical concept of affinity the following paper sets out to show how chemistry was always different from physics. Subsequently reference will be made to some facets of atomic theory in physics before the quantum theory. Finally it will be shown how history of quantum theory brought about a gradual rapprochement of the viewpoints of physics and chemistry.

The History of the Chemical Concept of Affinity. Relationality *Par Excellence*

"Combine the feminine with the masculine and you will find what you are looking for" [4]. This is an instruction by the famous alchemist *Maria* on how to produce certain substances; she probably lived in the first century *A.D.* [5]. Apparently in very early writings on *chrysopoeia* the chemical bond was understood as being analogous to a sexual unification of contrasts. The paradigm of alchemy in the early Middle Ages was – following on from such ideas – the synthesis of cinnabar from cold and damp mercury and hot dry sulphur [6].

From the mid 13th century a concept repeatedly turns up in alchemy – probably introduced by *Albertus Magnus* (†1280) – that we still find in chemistry nowadays, albeit in a much changed form: affinity. "*Sulfur propter affinitatem naturae metalla adurit*," wrote *Albertus* in *De mineralibus IV*: sulphur attacks metals because of its related nature. In the supplementary volume of the *Encyclopédie Diderot*'s from 1776 the significance of the former affinity is described as follows: "For a long time this expression had a vague and uncertain meaning which suggested a kind of sympathy, a truly concealed property, thanks to which various bodies are more or less easily unified."

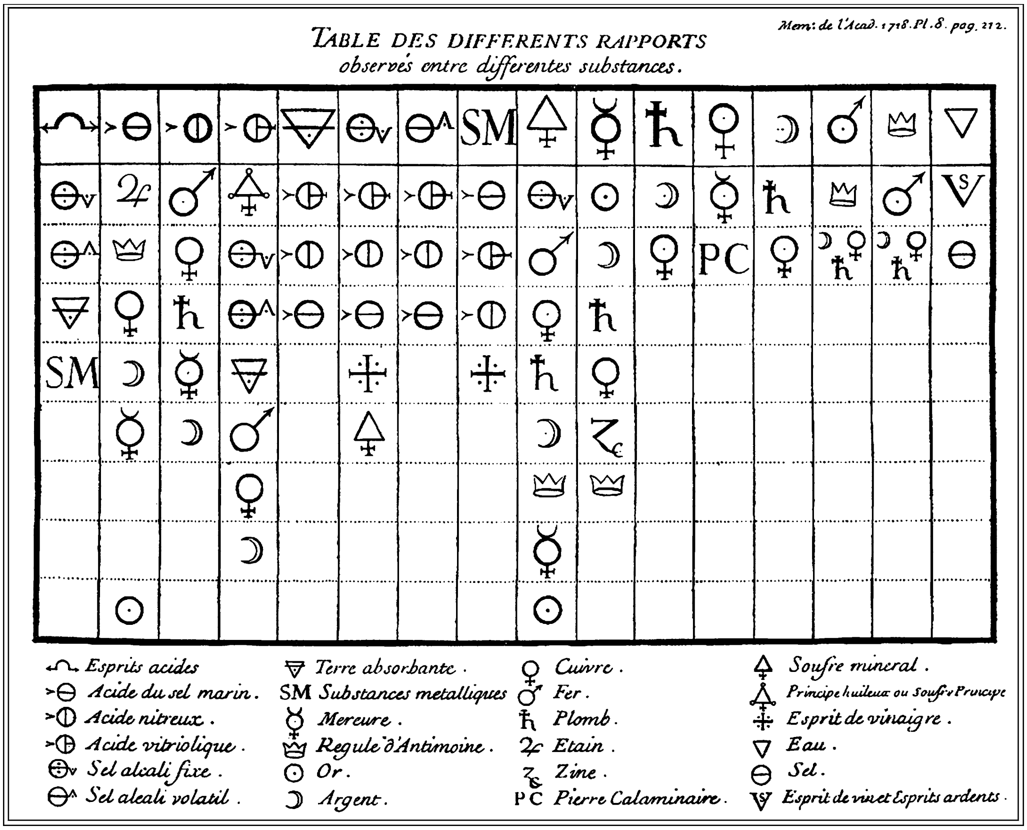
The Latin word *affinitas* means "relationship (through marriage)", "close bond (of two things)", whereby the relevant adjective *affinis*, consisting of *ad* and *finis* actually means "going to the limit", "standing close". Therefore when an *affinitas* is determined between two species, the conclusion is that these two things have a neighbourly relationship to one another. They exist somewhere in the same region and have at least one common border zone. Two things with an affinity to one another therefore have a relationship with one another.

The *Rosarium Philosophorum*, a collection of texts on alchemy from the 14th century, lists *affinitas* under seven peculiarities of substances, besides oiliness, fineness, dampness, purity, shininess, a consistent earthiness and the strength of colour [7]. *Affinitas* is defined as an adhesiveness when one substance encounters another, a "holding fast".

In this situation every attempt to create a system of order for the known (more or less pure) substances (acids, salts, metals, *etc.*) was most welcome. *François Geoffroy* sen. (1672–1732), who was first educated as an apothecary, then as a doctor and who became a professor at the University of Paris Etienne, went furthest in this respect. In 1718 he presented the Academy of Sciences with a table of relationships containing 16 columns and 9 lines. He called it the *Table des différents rapports observés entre différentes substances* (Fig. 1) [8].

In 1731, *Bernard de Fontenelle*, in his *Eloge* to *Geoffroy*, posed the question whether forces were concealed behind the affinities. In the early 18th century, when people considered forces, these were of course *Newton*'s forces of gravity which showed an interesting property for chemists: the planets are attracted by the sun but the planets also attract the sun. Chemists thought that chemical bodies should behave in a similar way by exerting a mutual attractive force over one another (Perhaps only an alchemist like *Newton* was able to discover the law of the mutual attraction of masses).

At that time the idea began to develop that chemistry was a science of combinations. All chemical properties are determined by forces (or by reactions released by these forces) among each other. It was along these lines that the Swedish chemist and mineralogist *Tobern Olof Bergmann* (1735–1784) analysed thousands of chemical reactions and summarised the results from 1775 in 49 columns. They contain 27 acids, 8 bases, 14 metals. The substances are listed in two tables: according to their reactions in a watery solution or "under the power of fire" [9].



Mem: de l'Acad. 1718. Pl. 8. pag. 212.

TABLE DES DIFFERENTS RAPPORTS
observés entre différentes substances.

⏜	>⊖	>⦶	>⊕	🜃	⊖v	⊖^	SM	🜍	☿	♄	♀	☽	♂	♔	▽
⊖v	♃	♂	🜏	>⊕	>⊕	>⊕	>⊖	⊖v	☉	☽	☿	♄	♔	♂	🜈
⊖^	♔	♀	⊖v	>⦶	>⦶	>⦶	>⊕	♂	☽	♀	PC	♀	☽ ♀ ♄	☽ ♀ ♄	⊖
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⏜ *Esprits acides*
>⊖ *Acide du sel marin.*
>⦶ *Acide nitreux.*
>⊕ *Acide vitriolique.*
⊖v *Sel alcali fixe.*
⊖^ *Sel alcali volatil.*
🜃 *Terre absorbante.*
SM *Substances metalliques*
☿ *Mercure.*
♔ *Regule d'Antimoine.*
☉ *Or.*
☽ *Argent.*
♀ *Cuivre.*
♂ *Fer.*
♄ *Plomb.*
♃ *Etain.*
ζ *Zinc.*
PC *Pierre Calaminaire.*
🜍 *Soufre mineral.*
🜏 *Principe huileux ou Soufre Principe*
🜊 *Esprit de vinaigre.*
▽ *Eau.*
⊖ *Sel.*
🜈 *Esprit de vin et Esprits ardents.*

Fig. 1. Table of affinities; *E.-F. Geoffroy, Tables des différentes rapports observés en chimie entre différentes substances* 1718

The historian Maurice Dumas said about Bergman that he "approaches his work with enthusiasm, as a conscientious craftsman, who hopes to gradually accomplish the immense task rising up before him. Apparently he planned to carry out all imaginable chemical reactions, compare their results and in this way classify the bodies in their relation to one another. [...] Seemingly he was not very satisfied with the results. He estimated that over thirty thousand exact experiments would be necessary to give his table a certain degree of completeness."

Bergman was particularly interested in the reactions of salts in aqueous solutions. Using the old symbols from alchemy he formulated the correct qualitative reaction equations of many double conversions of salts. *Bergman* was the first person to recognise the dual nature of salts (Fig. 2). After reading *Bergmann*'s work *De attractionibus electivis*, which was published in 1775, *Johann Wolfgang*

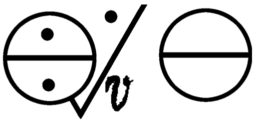

Fig. 2. Potassium chloride, participating in "pure fixed vegetable alkali" and "marinic acid", *T. Bergman, A Dissertation on Elective Attractions* 1785

von Goethe (1749–1832) was inspired to write his famous novel *Die Wahlverwandtschaften* (*The Elective Affinities*) in 1809. *Goethe* transfers the chemical pattern of reactions $AB + CD \rightarrow AD + CB$ into the sphere of human relationships.

Back to *Bergman*'s table of affinities: during research on the nature of forces behind affinity the French chemist *Louis Bernard Guyton de Morveau* (1737–1816) succeeded in making the next decisive step round about 1780. *Guyton de Morveau* measured the forces that are necessary to separate two metal plates swimming in mercury. He discovered that the forces adhere to the same sequential order as the chemical affinities.

We owe much to the doctor and chemist *Gabriel-François Venel* (1723–1775), who wrote the article *Chymie* in *Diderot*'s *Encyclopédie*, as well as other articles, for taking a great step forward in clarifying the question of chemical affinities. *Venel* aimed to put chemistry on an equal standing with physics. He succeeded in making a decisive first step in reconciling relational and non-relational aspects. According to *Venel* the components of a chemical aggregation engage in ‘‘neighbourly relations’’, whereby (formulated in today's language) he differentiates immutable atoms from mutable molecules. Every change has to be deduced from a change in the spatial arrangement of the corpuscle – rejection or attraction – without the particles themselves undergoing an inner change. *Venel* asked himself how therefore does gold become gold. Inner qualities specify the peculiarity of the body. These have the effect that water, gold, saltpetre, *etc*. are precisely water, gold, and saltpetre. The actual object of chemistry occurs in the mutual effects of the corpuscles on each other. These are dependent on the inner qualities of the particles [10]. *Venel* emphasises that the affinity that causes the mixtive unity of the aggregates has nothing to do with a gravitational attraction. However, in the same breath he says that even *Stahl*'s ‘‘principles’’ do not give an adequate answer to this question. The chemists who engage in chemistry as an enthusiasm, a crazy passion, have to be bold enough to admit their lack of knowledge in this respect.

For a very long time affinity was understood to be the force bonding the particles together as well as the direction in which a reaction goes. There was a famous controversy [11] between the chemists *Claude Louis Berthollet* (1748–1822) and *Joseph Luis Proust* (1754–1826) that ultimately led to the recognition that it was necessary to divide the concept of affinity into two differing concepts: 1. the strength of the bond and 2. the course of reaction in the sense of chemical balance. In most cases no immediate influence can be taken on the form of the bond but indeed on the course of reaction. In the following we intend to deal exclusively with the aspect of affinity in the sense of the bond of the species.

Atomic Theories in Physics in the 18th and 19th Centuries

Ruder Josip Bošković (1711–1787), who came from Dubrovnik in Croatia, can be regarded as the actual founder of a differentiated view of the formation and function of atoms [12]. *Bošković* introduced in *De viribus vivis* (Rome 1745) the concept of pointed mass. According to his theory atoms are mathematical points which emit rejecting or attracting forces.

The starting point for this consideration is the fact that atoms do not obey *Newton*'s laws. *Newton*'s formula $1/r^2$ can only be used for great distances.

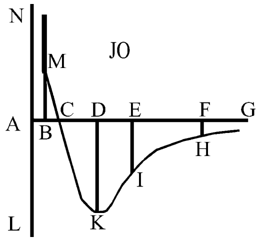

Fig. 3. Dependence of the force in the vicinity of a material point on distance; *J. R. Bošković*, *De viribus vivis* 1745, *figura 10*; forces above the horizontal axis are repulsive, those below are attractive; the letters identify points, where the repulsion turns into attraction, inflection points, the minimum, and so on

In proximity a force of rejection has to be predominant otherwise matter would be unstable. According to *Bošković*, interactive atoms are only physically imaginable if they are not impermeable. If there is sufficient attraction of the atoms, the amount of rejecting forces is almost infinite. The graphic illustrations of the strength of forces are known in being dependent on the distance of the atoms (Fig. 3). The curves are the same as those we find for the entire energy of a molecule dependent on the bonding distance in text books on quantum chemistry and is still valid nowadays!

During the first period he spent in Vienna (1756–1760) *Bošković* wrote his most important work *Philosophiae naturalis theoria* (Vienna 1758). In Part III of this book *Bošković* discusses the consequences of his theses for chemical transformations. To begin with, the author makes it clear that the primary elements of matter cannot be transformed (point 393). Studying chemical reactions demands an intimate knowledge of the structure of the individual particles and the geometric arrangement of all points of the mass (point 446). However, *Bošković* is of the opinion that this far exceeds the ability of the human intellect. Nevertheless the last observation does not prevent him from proposing an astonishingly far-sighted theory of the dissolution process of metals in acids (point 447): when dissolution occurs, the attractive force between the metal particles and the solvent is greater than that of the individual particles among each other. For *Bošković*, bonding between atoms (*i.e.*, chemical bonding in our sense) means the formation of a complicated pattern of force. According to *Bošković* the chemical species are complex structures and are the results of various forces.

Bošković's theory about the interactive impact of atoms had a considerable influence on the English chemist and physicist *Michael Faraday* (1791–1867), who, as is well known, came to the Royal Institution as a laboratory assistant to *Davy*. *Faraday*, while making his analyses of the nature of electricity, became interested at an early age for the *Bošković* theory. Beyond all doubt *Faraday*'s introduction of lines of force was inspired by *Bošković*'s theses.

Bošković and *Faraday* preferred to make a compromise between a pure idea of continuity and a discontinuous view of the structure of matter. At the same time *Dalton*'s atoms represented the purely discontinuous consideration.

On October 21, 1803, *John Dalton* (1766–1844) spoke before an audience of only seven people in the Literary and Philosophical Society in London about experiments to discover how gases are absorbed in liquids. He explained the

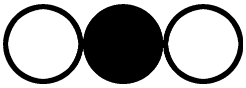

Fig. 4. Carbon dioxide: two oxygen atoms and one carbon atom, *J. Dalton, A New System of Chemical Philosophy* 1808/1810

behaviour of gases atomistically. *Dalton* was of the opinion that atoms were round and surrounded by a warming shell. They are immutable. Chemical operations extend only to the separation or unification of several atoms. Each bond consists of a certain number of atoms and can be formed in a ratio of whole numbers. In 1805 *Dalton* published his hypothesis about atoms and the first weight tables of atoms. In 1808 he published his work *A New System of Chemical Philosophy* [14] (Fig. 4).

In 1807, using a voltaic pile, *Humphry Davy* (1778–1829) succeeded in producing the elements sodium and potassium from molten caustic soda or caustic potash. *Davy* was convinced that the key to the understanding of chemistry and in particular to the understanding of affinity was to be found in electricity. But what is electricity?

Considerable progress was achieved when the Swedish chemist *Jöns Jacob Berzelius* (1779–1848) took up *Davy*'s theory. *Berzelius*'s words were programmatically contained in volume II of his textbook printed in 1812. In the section "The essential features of a future electro-chemical theory" he arrived at the conclusion, "that what we call affinity and all its variations is nothing other than the effect of electrical polarity of particles and that electricity is the *primum movens* in all chemical interactions. It is the origin of light and warmth…"

Taking as his starting point the experimental results of the electrolysis of smelting salt, *Berzelius* interpreted the affinity of substances as the intensity of their polarity. *Berzelius* differentiates between "electro-positive and electro-negative elements". Potassium is his most electro-positive, oxygen his most electro-negative element, whereby he understood an electro-positive element to be one "in which the positive pole predominates". In the case of an electro-negative element "the negative pole has the upper hand". In any case *Berzelius* was able, through his hypothesis, to clarify a variety of findings in chemistry and establish a comprehensive dualistic system.

Subsequently, however, it became evident that *Berzelius*'s "specific unipolarity" alone could not explain all the observed phenomena and especially not the degree of affinity of chemical bodies. *Berzelius* was compelled to introduce the intensity of polarisation as an additional factor, *i.e.*, to be more precise, polarisation ability. For instance, he argued that oxygen bonds more readily with sulphur than with lead because sulphur's positive pole can neutralise a larger amount of negative electricity of the oxygen pole. What we now consider to be a strange idea about the cohesion of molecules was the extent of findings around the mid-19th century.

The Gradual Rapprochement of the Viewpoints of Physics and Chemistry

Physicists increasingly arrived at the realisation that the special conformity to a natural law in chemistry can only be described with a concept of atoms when the complex interactive mechanisms of atoms are taken into consideration. On the other hand, leading 19th century chemists soon rejected the idea of establishing relations too rigorously. They were committed to the unit construction principle. *Liebig* and *Wöhler*'s radical theory consisted of asserting that carbon, hydrogen, and oxygen can form groups: in organic species these groups behave like the various elements in inorganic chemistry. However, why atoms should collect in groups and form molecules, remained unclear.

Josef Loschmidt (1821–1895), who was born in the small village of Putschirn near Karlsbad in Bohemia, refers in the first paragraph of his *Chemical Studies I* from 1861 to an idea of the atom that corroborated that of *Justus von Liebig*; namely that there are large empty spaces between the atoms [15]. *Loschmidt* imagines atoms as centres of a rounded effect of attracting or repelling forces, whereby "strictly speaking, the sphere of action of an atom is unlimited."

In the graphic depiction of atoms *Loschmidt* decided to more or less cut off the sphere of action of an atom arbitrarily in the case of a "moderate diameter" in the form of a rounded surface (which brings to mind a certain orbital representation). According to *Loschmidt*, when molecules are formed, both spheres are permeated and *Loschmidt* speaks about a "crossing through". In the case of double bonds the spheres permeate each other more strongly; permeation reaches a maximum in the case of a triple bond. In a few paragraphs *Loschmidt* presents us here with an almost clairvoyant idea of the structure of the molecule. His depictions of molecules correspond to what is nowadays known as molecular modelling (Fig. 5).

Loschmidt was here following the ideas of *Johann Friedrich Herbart* (1776–1841), whose works he studied in Prague in the house of his teacher *Franz Exner*. In 1829 in Königsberg *Herbart* published his *General metaphysics besides the beginnings of the philosophical doctrine of nature*. *Herbart* adopted the view – following *Bošković*'s theses – that atoms were in no way to be comprehended as hard balls but as spherical structures attracting and repelling each other whereby they partially permeate each other. In so doing these species – he referred to them as "elements" – followed certain structural laws of nature. "If, for example, several bodies of type A simultaneously come into an incomplete conjunction with a real body of type B, they must all penetrate more or less deeply into B [...] but the more of them there are, the less deeply they can penetrate into B, because B can only absorb a limited number. If then they all penetrate to a certain degree, so they must all be simultaneously driven out in all directions, so that attraction and repulsion are in equilibrium. Then B (as the central atom) would lie in the middle and, taken together with all of A, would occupy more than one mathematical point, so that a physical space would develop and the whole then represents a small cluster or molecule." [16]

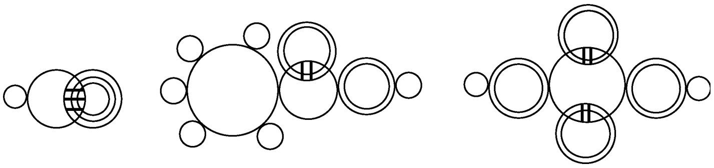

Fig. 5. Hydrocyanic acid, benzoic acid, and sulfuric acid; *J. Loschmidt, Chemische Studien I* 1861

Now to the nature of forces which keep atoms together in larger units of atoms. In 1881, in what became a famous *Faraday* Lecture, the German physicist *Helmholtz* came to the conclusion that whatever chemical affinity may be (here he meant chemical bonding), it would have to be electric in its nature. In the case of salt-like affinities such as KCl or HF this was also easily imaginable. But nobody had any idea how this electricity could contribute to bonding in species such as O_2 or Cl_2.

In 1897, in the *Cavendish* Laboratory in Cambridge the English physicist *Joseph John Thomson* (1856–1940) determined the relationship between mass and charging of the electrons emerging from a cathode of a cathode radiation tube. This did not yet lead to much. Where did this electron come from? In 1904 *Thomson* developed the first electronic theory of valency. This was a mixture of the electro-chemical diagram of *Berzelius* and *Maxwell*'s equations for electromagnetic phenomena. A bond should come about by atoms giving off one or several electrons to other atoms. *Thomson*'s theory was purely electro-static, whereby it postulated a polar character of all bonds.

Likewise in 1904 the German electro-chemist *Richard Abegg*, who was born in 1869 and killed in a ballooning accident in 1910, formulated a kind of rule of eight for the elements of the second and third period of the PSE: the law of valency and contravalency. The American chemist *Gilbert N. Lewis* (1875–1946) had similar ideas two years earlier, when during a stay in Manila he had the opportunity to think about various things. At that time he scribbled a series of "cubic atoms" from the first eight row period of the period system on the reverse of an envelope, whereby in the case of lithium only one electron occupied one of the eight corners; for fluoride on the other hand seven electrons were allocated places [17]. In 1916 the German physicist *Walter Kossel* referred to the fact that atoms use their outer electrons (the valency electrons) in order to form hetero-polar chemical bonds and thereby take on the electronic structure of the nearest inert gases (inert gas rule). In the same year *Lewis* presented his octet rule. *Lewis* was the first person to understand that atoms do not necessarily have to exchange valence electrons. They can share two, four, or six electrons and thereby achieve a co-valent bond, whereby in the first case a simple, in the second a double, and in the third a triple bond is the result. *Irving Langmuir* from New York, a pupil of *Nernst* and later a *Nobel* prizewinner initially gave publicity to the *Lewis* Theory of Common Pairs of Electrons but it was not until 1923 that *Lewis* wrote his masterpiece *Valence and the Structure of the Atom*. On page 79 we find the essence of the theory in three sentences (*Lewis*'s italics): "The new theory, *which includes the possibility of complete ionisation as a special case*, may be given definite expression as follows: Two atoms may conform to the rule of eight, or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons. The electrons which are held in common by two atoms may be considered to belong to the outer shell of both atoms."

The *Lewis* Theory was very successful. It was finally possible to interpret the old chemical bonding dashes, whereby we must recall the pioneers of structural chemistry *Archibald Scott Couper* (1858), *Josef Loschmidt* (1861), *Alexander Crum Brown* (1864), and *August Kekulé* (1865). Nevertheless *Lewis*'s concept contained two indisputable flaws. 1) It could not predict the existence of the molecule

H_2^+. 2) It could not be quantified. It could not be used at all for making calculations. It was actually a rule that considered extensive material of chemical experiences.

Nothing could be calculated with the pairs of electrons because the physics behind the theory had not yet been discovered. It was not clear why pairs of negatively charged electrons should somehow stay together. According to classical electro-statics, particles charged in the same direction must to repel each other. How far had physics arrived by 1916? The answer is simple: quantum mechanics was still in its infancy. It was the time of the old quantum mechanics and still before the uncertainty principle. At that time no one had yet discovered the spin of electrons.

Before we come to important discoveries made at the beginning of the 20th century, I'd like to include at this stage a less well known story that occurred around 1909/1910 in Vienna. *Arthur Erich Haas*, born in 1884 in Brno, applied at the beginning of 1909 for authorisation to teach the history of physics at the Faculty of Philosophy at the University of Vienna and submitted a scientific-historical thesis [18]. Initially the committee of professors was completely baffled. Who was to assess this kind of work? *Haas*'s application was rejected and he was informed that he should submit a work of physics as his postdoctoral thesis. In order to meet this requirement *Haas* studied the most recent literature on physics: *Planck*, *Thomson*, *Rayleigh*, *Lorentz*.... In *Planck* he read about mysterious oscillators and about the quantum of action *h*. *Arthur Erich Haas* could only imagine these oscillators as atoms. At the end of 1909 he set to work and undertook "an attempt to make an electro-dynamic interpretation of *Planck*'s quantum of action". The aim was to establish a formula that related the constant *h* to the basic rules of the electron theory. *Haas* thereby set up a formula for the radius of the most simple atom, hydrogen. He compared the potential energy of the electron with *Planck*'s energy $h\nu$. As a result *Haas* also found the first interpretation of the *Rydberg* constants. Ultimately, from the *Rydberg* constants he calculated an atomic radius a, that he stated as to be 1.88×10^{-8} cm (*cf.* the *Bohr* radius $a_o = 0.529 \times 10^{-8}$ cm).

Looking back on his life *Haas* wrote, "To begin with in Vienna people took little notice of me. In February 1910, when I gave a lecture about my work in the Viennese Society of Chemistry and Physics, *Lecher* thought he was being particularly funny in the public discussion when he referred to the whole thing as a carnival joke. When *Laurenz Müllner* (the philosopher) asked *Hasenöhrl* about me, he explained that I could not be taken seriously because I naively combined branches of knowledge that have absolutely nothing to do with one another such as quantum theory (as something about the theory of warmth) and spectroscopic analysis (as something optical). It is understandable that I was deeply discouraged by this".

In 1913 *Haas* was appointed professor of the history of physics in Leipzig and from 1921 he was professor of physics in Vienna. In 1936 he went to the USA to the University of Notre Dame, South Bend, Indiana. He died on February 20, 1941, in Chicago. *Haas* was not only the first person who attempted to apply quantum theoretical laws to the structure of atoms but in 1929 *Haas* was also the first person to refer to quantum chemistry. He had obviously advanced his ideas too soon as in 1910 the time was not yet ripe for it.

A British physicist from New Zealand, *Ernest Rutherford* (1871–1937), who liked to regard himself as an alchemist, stimulated the discussion about atomic structure round about 1911. In 1931 he was ennobled and became Lord *Rutherford*. A woodcut hung over *Rutherford*'s desk in Cambridge and portrayed the scene in an alchemist's kitchen; he owned literature on alchemy; one of his books is entitled *The New Alchemy*. An alchemistic "crocodile" (actually the ouroboros) is still carved into the wall of his laboratory. It was at the instigation of *Piotr Kapitza*, a student of *Rutherford*, that the famous artist *Eric Gill* put it there. *Rutherford*'s first study, the identification of α-rays as the nuclei of helium atoms that leave an unstable nucleus of an atom, was basically related to the awareness of the possibility of making a transmutation of chemical elements. Incidentally the radium specimens that *Rutherford* had at his disposal for his experiments, came mainly from the St. Joachim valley in Bohemia. In 1907 they had been isolated from pitchblende in *Auer von Welsbach*'s factory by the chemists *Ludwig C. Haitinger* and *C. Ulrich* in Atzgersdorf near Vienna [19]. In 1911 *Rutherford* felt compelled to postulate the existence of an atomic nucleus. In 1919 he recognised the first "artificial" nuclear reaction: when atomic nuclei of nitrogen are bombarded with α-rays they are transformed into atomic nuclei of oxygen, thereby releasing a proton. This was the first real *transmutatio specierum* that the alchemists had spent 2000 years searching for.

From 1911 to 1913 the Danish physicist *Niels Bohr* (1885–1962) worked as a member of *Rutherford*'s staff in Cambridge. In 1913 *Bohr* had a surprisingly great success with the interpretation of the hydrogen spectrum: electrons move free of radiation along circular orbits around the atomic nucleus and possess a characteristic energy W_n. In the case of leaps between the orbits the differential amount ΔW is reflected as a light quantum. However, when *Bohr* wanted to go on to describe atoms with several electrons, it became surprisingly complicated. *Arnold Sommerfeld* (1868–1951) in Munich took over the generalisation of the rule of quantisation. In 1922 *Bohr* was able to explain the architecture of the periodic system of the elements by allocating electrons to certain orbits.

Bohr's orbit allocations were – at least until the 6th period – accurate. In 1922/1923, following the ideas of the fan-shaped arrangement of the elements by *Thomas Bayley* and the Danish chemist *Hans P. J. J. Thomsen* (1826–1909), *Bohr* set up a period system of chemical affinity according to his ideas. *Bohr* was able to state the correct positions of the empty places for the elements 43 (later technetium, Tc), 61 (prometium, Pm), 72 (hafnium, Hf), and 75 (rhenium, Re) and reserved free places left for the 5f elements. According to *Bohr*'s statements, element 72 should not belong to the rare earths. It is supposed to be similar in its chemical properties (*e.g.*, stages of oxidation) to zirconium. At that time there were already reports about the discovery of element 72, including a report by *Urbain*, who called the element celtium even though *Moseley* had not been able to find it in his samples. A specific search was undertaken in *Bohr*'s institute. Only a year later *Bohr*'s friend, the Hungarian physicist and chemist *Georg von Hevesy* (1885–1966) and the Dutch X-ray spectroscopist *Dirk Coster* (1889–1950) were able to announce the identification of element 72 in zirconium ores. They called it hafnium [20].

Then great advances were made. Early in 1925 *Wolfgang Pauli*, born in Vienna (1900–1958) after studying the anomalous *Zeeman* effect, formulated the exclusion principle: two electrons with identical quantum numbers cannot exist in one atom. In November 1925 two Dutch physicists, *G. E. Uhlenbeck* (1900–1988) and *S. A. Goudsmit* (1902–1978), discovered the spin of electrons which helped to explain the 4th quantum number. The German physicist *Friedrich Hund* also recognised in 1925 the rule of maximum spin multiplicity.

In May of the same year during a stay on the island of Heligoland *Werner Heisenberg* elaborated the basic features of his matrix mechanics, which he published later with *Max Born* and *Pascual Jordan*. In January 1926 *Erwin Schrödinger* (born on August 12, 1887, in Vienna, died on January 4, 1961) wrote the first paper of his four ''Mitteilungen zur Wellenmechanik''. *Schrödinger* took up *Louis Victor de Broglie*'s idea of electron matter waves. In Schrödinger's wavefunction Ψ – at first he called it *feldskalar* – the quantisation resulted almost automatically. The energy levels of the hydrogen atom were produced as three-dimensional analogies to the specific frequencies of a vibrating string [21].

In February 1927 *Heisenberg* wrote a letter to his friend *Pauli* reporting a new interesting discovery: when attempting to describe the collision between two electrons, the variables p and q that represented the impulse and the position of the electrons, behaved strangely. As soon as one took control over one of the two sizes, it had to be accepted that the other was ''out of control''. *Heisenberg* had recognised the uncertainty. When taking readings it is impossible to do justice at the same time to the wave and particle character of objects. *Niels Bohr* summarised this realisation in July 1927 in the concept of the ''complementary principle'' [22].

What came afterwards is occasionally subsumed under the motto ''grieving'': quantum mechanical objects are determined by the experimental arrangement in their properties. Each reading is interactive. It is impossible to determine the properties of isolated objects. Electrons near to atomic nuclei are anything but isolated objects.

While several physicists were preoccupied with the interpretation of their findings, *Walter Heitler* (1904–1981) and *Fritz London* (1900–1954) published the first quantum mechanical calculation on the molecule H_2 [23]. 1927 was the birth hour of the theory of chemical bonding on a quantum mechanical basis [24].

The first phase of quantum chemistry that lasted from 1927 to 1935 was characterised by the fact that attempts were made to understand the known rules of the classical valence theory in a quantum theoretical manner and make them plausible. Scientists did not try to deduce statements about the structure and properties of molecules from the quantum theory. At that time this approach was still far too difficult. As a way out of this problem *Linus Pauling* (1901–1994) suggested the introduction of the concept hybridisation. In a series of essays and in his textbook *The Nature of the Chemical Bond*, Pauling put forward the Valence Bond (VB) Theory. At the same time *Friedrich Hund* and *Robert Mulliken* (1896–1986) made efforts to understand the spectra of molecules with two atoms. They were able to show that a description of a molecule by molecular orbitals (MOs) was a very good approach. The so-called correlation diagrams proved to be useful for the qualitative understanding of MO energies. *Lennard-Jones* suggested representing molecular orbitals as linear combinations of atom orbitals: the LCAO-MO-Method. In 1932 *Nevil. V. Sidgwick* (1873–1952) extended the concept of co-valent bonding to complex metal affinities [25]. *H. Bethe*, *R. Schlipp*, *W. Penney*, and *J. van Vleck* recognised the meaning of the d-orbitals of metallic central atoms. This was the basis for the crystal field theory which was not replaced until the 1950s by *Leslie Orgel*'s ligand field theory. It was only at this late stage that MO theoretical principles were reconciled with the crystal field theory that is based on electrostatic argumentation.

In 1933 the German physicist *Hans G. A. Hellman* (1903–1938) was the first person to recognise the nature of the quantum mechanic effect that leads to chemical bonding: when separate atoms come together to form a common molecule, the space available to the electrons is enlarged; the uncertainty of the position function increases. This implies a reduction of impulse uncertainty. As the central impulse is zero, smaller impulses become more probable which leads to a reduction of the kinetic energy of the electrons [26].

Hans G. A. Hellmann should probably be regarded as the actual founder of quantum chemistry. He was born on October 14, 1903, in Wilhelmshaven and studied between 1922 and 1929 in Stuttgart and Kiel with *Kossel* and *Ewald*. In Kiel he worked on the verification of the *Debye-Hückel-Onsagen-Falkenhagen* theory of dielectric constants. *Otto Hahn* and *Lise Meitner* supervised his doctoral thesis in Berlin. He married *Victoria Bernstein*, a Jewish-Ukrainian orphan. His son *Hans* (*H. Hellmann* jun.) was born in October 1929. In the same year *Hellmann* took up an appointment at the Institute of Technology in Hannover. In 1933 he worked among other things on the problem of the geometry of the NH_3 molecule, on a molecular virial theorem, and on the *Hellmann-Feynman* theorem. *Hellmann*, together with the young physicist *W. Jost*, wrote an essay on the fundamental ideas of quantum chemistry and chemical bonding for the *Zeitschrift für Elektrochemie*. His application to become a lecturer was rejected in 1933 and on December 24, 1933, he lost his position as assistant professor because his wife was Jewish. He was offered a post at the *Karpov* Institute of Physical Chemistry in Moscow and so *Hellmann* left his homeland and emigrated with his family to the Soviet Union where, in 1934, he completed his work on pseudo potentials. He was working at that time on his textbook of quantum chemistry that was first printed in Russian at the beginning of 1937 as *Kvantovaja Khimija* in Moscow. After revising the work it was published in German in the same year, 1937, by Deuticke in Vienna and entitled *Einführung in die Quantenchemie* (*Introduction to Quantum Chemistry*). In March 1938 *Hellmann* was arrested in Moscow on the pretext that he was spying for Germany and only a few weeks later, after no legal proceedings, he was shot – according to the most recent research in the archives – on May 29, 1938, in the Taganka prison. Many years later his wife was informed that her husband had died in prison of an infectious disease [27].

The next phase of quantum chemistry covers the period from 1935 to 1950. Around 1935, without taking *Hellmann*'s findings into consideration, indeed even in opposition to his correct approach, it was generally regarded that the problem of chemical bonding had in principle been solved. If scientists had been more honest, they would have had to see that only the questions that could be solved by intuition and consideration had been exhausted – in any case that is how *Werner Kutzelnigg* once formulated it [28].

A third phase in quantum chemistry began around 1950. Computer technology had meanwhile made such great progress that solutions to problems could be attempted that would have earlier failed because so many calculations were necessary.

New classes of substances were then discovered whose treatment as part of the classical valence theory would have been impossible: *e.g.*, the boron-hydrides and the metal aromatic complexes. Such bonds were produced that theory had failed to predict. (We are talking primarily here about noble gas compounds.)

Taking the *Sidgwick-Powell* rules as a starting point, according to which the form of a molecule is dependent on the number of pairs of electrons in the valency shell, between 1957 and 1961 the Australian *Ronald Nyholm* (1917–1971) and his American colleague *Ronald Gillespie* (born in 1924) refined the approaches to yield a sophisticated possibility of predicting molecular geometries. Their ***V****alence* ***S****hell* ***E****lectron* ***P****air* ***R****epulsion* (VSEPR) theory makes it possible to state the most complex quantum chemical natural laws using a primitive rule [29]. This posed the question as to how something like this was possible. How do the simple bonding lines of chemical formula fit together with the complicated results of MO calculations?

From 1962 such questions about the chemical interpretation of the results of calculations played an increasingly important role [30]. In 1960, during a special lecture *Mulliken* formulated the question, "What are the electrons really doing in molecules?". The question was answered after preliminary studies [31], for example by *K. Ruedenberg*, *G. Edmiston*, *S. F. Boys*, and *W. Kutzelnigg*. It became evident that the often strictly localised description of molecules by their valency formula is equivalent to the largely de-localised representation in canonic molecular orbitals. It is possible to go from one description to another [32].

By localisation processes, molecular orbitals can be transferred to localised pairs of electrons (lMOs) in the sense of bonding dashes. To a certain extent the knowledge of this equivalence represents the conclusion for the time being of a long foreseeable rapprochement of the viewpoints of chemistry and physics: Chemical species should always be considered as the result of an interference – or as one may also say – of an interaction.

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