

Translated from Bunsen - Magazin 1999 (1) 10-21, (2) 60-70
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Hans G.A. Hellmann (1903-1938) ¹⁾

Part I. A Pioneer of Quantum Chemistry

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*The history of great scientific discovery is the story
of the disappearance of human prejudice under the weight
of experimental evidence [...]
The incorruptible guardian of the progress of our knowledge
is testing our experience against statements established
by mathematical theory.*

Hans Hellmann [H30]

Hellmann was a theoretical physicist with an excellent knowledge of chemistry.
His most important, lasting achievements are:

1. Pioneering contributions to the physical significance of covalent bonding
2. The molecular virial theorem and description of its consequences
3. The quantum mechanical force theorem (Hellmann-Feynman Theorem)
4. The "combined approximation method", today's pseudopotential or effective core potential method
5. The formalism of diabatic and adiabatic elementary reactions
6. The textbooks on "Quantum Chemistry"

¹⁾A "Hellmann-Archive" was created in Siegen in commemoration of Hans Hellmann. This is where documents on the biographical details can be found. Correspondence with further details and materials are welcome at the correspondence address below. We should be most grateful to receive comments from our readers, especially with regard to Hellmann's scientific effect, and also for additions to our Hellmann archives, particularly as we are presently engaged in a complete biography incorporating also historic and socio-political details. The Hellmann-Archive contains also copies of all papers of Hellmann. They are listed in the Appendix.

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Hans Hellmann and His Fate

For more than half a century the fate of one of the great pioneers of quantum chemistry lay hidden in darkness. The political upheavals in socialist states in the late 1980s have enabled some light to be shed on this matter. We can now give a preliminary summary of our scientific and historical researches in order to maintain the memory of Hans Hellmann's achievements for the scientific community. He was born in Wilhelmshaven (north-west Germany), and his publications were mainly in German, but later also in Russian. After he had had no choice but to emigrate from National Socialist Germany to the Soviet Union, he was finally liquidated in 1938 by the "Real-Socialists" and then passed over in silence for a long time.

1. Grounding in Wilhelmshaven, Kiel and Stuttgart (1903-1929)

1.1 *Childhood, School and Basic Studies*

Hans Gustav Adolf Hellmann was born on the 14th of October 1903 in the seaport town of Wilhelmshaven in north-west Germany as the first of two children. His parents were a non-commissioned officer in the navy, Gustav Diedrich Hellmann, and Hermine Anna Bernhardine Hellmann, née Hasse. The background of the family was in smallholdings and manufacturing work in north-west Germany. While Hans was still at elementary school, his father died in a traffic accident. His mother eked out her meagre pension with earnings from midday meals served to working men in her own home. Thus Hans was able to attend the classical grammar school in Wilhelmshaven and obtained the higher leaving certificate at Easter 1922. He earned his own pocket money as a local tourist guide.

At this economically difficult time after the first World War it seemed sensible for Hellmann to learn something "practical". After the appropriate manual training he enrolled for the winter term 1922/23 at the Institute of Technology in Stuttgart for electrical engineering. However, by the next summer term, following his inclinations, he changed to the more theoretically aligned »technical physics« department. He financed his studies partly through work at the workshops and laboratories of the wharves in his home town. Nevertheless he found time, as was then common, to join a students' association (see *Fig. 1*). After a total of four semesters he took one semester's leave of absence to work as a private tutor. During this period he had the leisure to prepare himself for the preliminary physics diploma.

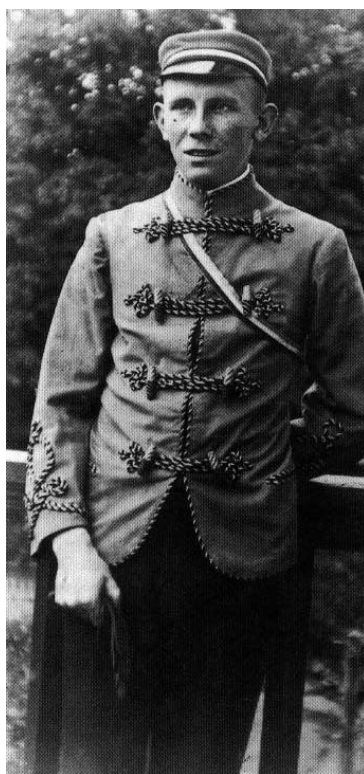


Figure 1: Hellmann as a student

1.2. Applied Physical Chemistry for a Livelihood: Experiments on Electrolytic Solutions²⁾

In the following summer semester 1925 we find Hellmann at the University of Kiel. Among other lectures he heard Professor Walther Kossel, no doubt for the first time about the electronic theory of valency. The main purpose of the Kiel semester was, however, to work as a student assistant in the laboratory of experimental physics, run by Professor Hermann Zahn, on a topic from the field of physical chemistry. This research was supported financially and with equipment by the Reich Navy and the "Emergency Association of German Science" (a forerunner of the "German Research Foundation", DFG). It concerned the measurement of the frequency dependent dielectric constants of conducting hydrous salt solutions (see *info-box* below). Hellmann's original ideas in his contributions between 1925 and 1934 [H1-H7, H15, HC15] occurred during the turbulent period of the theory of strong electrolytes developed by Peter Debye, Erich Hückel, Lars Onsager and Hans Falkenhagen in the years from 1923 to 1932.^[1] The details of charge distributions of ionic clouds in solutions, and their relaxation processes determining the permittivity as a function of electrolytic concentration and frequency of the electric field, were to be tested.

Hellmann's experimental work was characterized by extremely careful execution of difficult procedures. He continued this work later at Hannover (see below sect. 2.9), when his research was already concentrated on quantum chemistry. He also set an example by his work on the theory of electrochemical measurement techniques. His far-reaching research into all sources of error allowed him, even then, to obtain measured results of the correct sign and order of magnitude (even to one-percent accuracy, see *Fig. 2*), which not all pioneers of the time were fortunate enough to achieve (cf. Walden, Ulich, Werner^[2] and [H5, H6]). This high precision enabled scrutiny and confirmation of an important kinetic aspect of the theory of strong electrolytic solutions. Later research^[3] confirmed the earlier findings by Hellmann and Röver [H15, HC15]. It is only recently and thanks to the development of microwave spectroscopy that these properties can be measured reliably and accurately in the corresponding frequency region and that important knowledge about structure and dynamics of electrolytic solutions can be established.^[3a]

Hellmann's Procedure to Determine the Frequency Dependency of Dielectric Constants

Hellmann's method was to measure the intensity I of a standing radio wave on a "Lecherparalleldrahtsystem". The standing wave was formed between the surface of the electrolytic solution and the short-circuited end of the "Lechersystem" after which, through raising or lowering the level of the liquid, it was tuned into the resonance frequency. I , at the fixed position of maximum intensity, depends only on the reflexion coefficient R of the electrolytic solution:

$$I = \text{const} \cdot \{(1 + R)/(1 - R)\}^2$$

where

$$R^2 = (\mathbf{h} - 1)/(\mathbf{h} + 1)$$

is given by the complex permittivity

$$\mathbf{h}(\mathbf{l}) = \boldsymbol{\epsilon}(\mathbf{l}) - i\mathbf{k}(\mathbf{l})/2\mathbf{p}c\boldsymbol{\epsilon}_0 .$$

$\boldsymbol{\epsilon}$ is the dielectric constant or dielectric dispersion of the electrolytic solution at wavelength \mathbf{l} , \mathbf{k} denotes its specific conductivity and c the speed of light. (The dielectric loss plays a significant role only when the wave lengths λ are shorter than those applied here.)

1.3. Graduation in Physics: Experimental Atmospheric Chemistry

For the next seven semesters Hellmann again studied at Stuttgart, under Professors Ewald, Regener, Fues and others. One may suppose that those named, who later, for instance, tried to obtain a lectureship for Erich Hückel at Stuttgart, would have informed their students about the exciting results of the newly created quantum mechanics and its application to molecules and crystals. This must have made an impression on Hellmann. First, however, after a short time training under Otto Hahn and Lise Meitner at the Berlin "Radioactive Laboratory", he passed his physics graduation examination with distinction. It included experimental work on the "synthesis of radioactive preparations for physical research". Shortly before that, Hellmann was one of the first to be admitted to the "Württemberg Regional Association of German Physicists", founded by Erich Regener.

²⁾ The citations ^[n] refer to the general list of references, and [Hn] and [HCn] to Hellmann's bibliography in the Appendix.

After graduation Hellmann became practical assistant to the experimental physicist Erich Regener, who had many and varied interests.^[4] In May 1929 he obtained his doctorate under the auspices of Regener, his thesis being "On the Occurrence of Ions from the Decomposition of Ozone, and the Ionization of the Stratosphere". At that time there was speculation about the origin of charge carriers in the stratosphere. In particular it was suspected that pairs of ions appeared when ozone decomposed. Hellmann was able to show, however, that markedly fewer than one pair of ions were formed per 10^{15} molecules of ozone. This work also showed special care in carrying out and interpreting difficult laboratory experiments, so that despite the limitations of measurement technology at that time, it was possible to obtain admirably accurate results. Hellmann also helped his professor with the analysis of critical data in other projects [H8].

1.4. Marriage with Political Consequences

The relationship of Professor Regener with his students was decidedly friendly.^[4] After invitations to Regener's home, Hans Hellmann became acquainted and fell in love with the Regeners' charming foster daughter Viktoria Bernstein (see Fig. 3), a distant relative of Regener's wife Viktoria, née Minchina. (Both Viktorias came from Ukrainian Jewish families, a fact which was later to have dangerous consequences for both men, particularly for Hans Hellmann). Viktoria Bernstein's parents had both died early, and she was finally able to leave the Soviet Union in 1922 after the First World War and the Revolution and seek shelter with her aunt in Stuttgart. There she was trained as a children's teacher. Shortly after Hellmann's doctorate, at the beginning of January 1929, he and Viktoria were married.

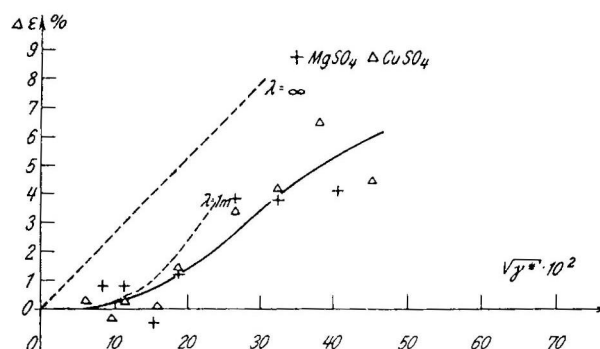


Figure 2: Percentage increase $\Delta \epsilon$ of the Dielectric Constant (i.e. the real part of the permittivity) of hydrous salt solutions ($MgSO_4$, $CuSO_4$) at 270 MHz, versus the root of the equivalent concentration g^* in Mol/l. (+, Δ): measured by Röver, a candidate for a doctor's degree studying under Hellmann, at a wavelength of 1.1m, and (-----): calculated according to the Debye-Falkenhagen theory for a stationary field ($\lambda = \infty$) and for 1m waves ($\lambda = 1m$). Some data of other authors were omitted from the original diagram [HC15, Fig.11] for clarity.

2. Lectureship in Hannover (1929-1934)

2.1. The Change to the Newly Developing Discipline of "Quantum Chemistry"

At this time, Professor of theoretical physics Erwin Fues, mentioned above, was called from Stuttgart to the Institute of Technology (TH) in Hannover. He offered Hans Hellmann an assistant's post, and thus the latter could finally carry out his intention to apply quantum mechanics to the problems of theoretical chemistry. Hellmann started work on the still new area of "Quantum Chemistry", whose birth^[5,6] was marked by the work of Heitler and London in 1927.^[7] In 1928 this area was still called "mathematical chemistry"^[8] or "sub-atomic theoretical chemistry",^[9] later also "chemical physics".^[10] The phrase "quantum chemistry" seems to have been used for the first time in 1929 in Arthur Haas' lecture to the Viennese Chemical-Physical Association.^[11] The fact that quantum chemistry at that time was a particularly topical subject is confirmed by the Annual General Meeting 1928 of the German Bunsen Association ("Types of Chemical Bonding and the Structure of Atoms"),^[12] further by the "Leipziger Woche" initiated by Debye ("On Problems of Quantum Theory and Chemistry");^[13] it was also topical at meetings of the English Faraday Society ("Molecular Spectra and Molecular Structure")^[14] and of the American Chemical Society in the same year ("Symposium on Atomic Structure and Valence").^[15]

2.2. Problems with Principles of Quantum Mechanics: Does Spin exist?

At first, however, Hellmann devoted himself to a burning question of current interest, posed by Prof. Fues, which was then controversial: were there spin-polarized electron waves, that is, have free electrons in space four or only three degrees of freedom? Shortly before, Bohr and Mott had suspected and reliably proved the impossibility of a Stern-Gerlach experiment for *free* electrons.^[16] Does spin perhaps only exist as an additional and two-valued degree of freedom for atoms and molecules? Fues and Hellmann [H10] were able to solve the problem through a thorough discussion of Dirac's equation: there *are* spin polarized free electrons. In particular they proposed experiments to test this.

A related, similarly controversial contemporary problem was that of whether spin-polarization of unpolarized electrons by an electric potential was, in principle, possible, as was the view of Weisskopf^[17] and Hellmann [H11, H12], or whether the opposite was the case, as suggested by W. Pauli and Th. Förster.^[18] The negative results of many experiments made in this direction even raised doubts as to the correctness of the Dirac equation,^[19] on which basis Mott had shown that polarization of spin is generally depended on the shape of the potential, on the electron's speed and on the scattering angle. Hellmann was later able to correct his own calculations (which had revealed at least a mathematical sign error in the experimental results) see [H12] and which elegantly confirmed the results of Th. Förster's specially treated case [H23].

2.3. Contacts with Chemists: Chemical Bonding as an Electrostatic Phenomenon

By far the most strongly represented discipline at the Faculty of General Science of the Hannover TH was chemistry. Thus Hellmann found the atmosphere conducive to discussion of his own main project, the clear quantum mechanical description and interpretation of chemical bonding. Amongst others he had contact with inorganic chemists, the director Prof. Wilhelm Biltz, the senior lecturer Wilhelm Klemm and the assistants Werner Fischer,^[20] Wilhelm Geilmann and Robert Juza, with organic chemists, the assistant Fritz Keil and the senior lecturer Günter Schiemann, and with physical chemists, Prof. Hermann Braune and senior lecturer Wilhelm Jost [H16, HC16]. Of course he also exchanged ideas with the physicists, with the experimental physicist Prof. Precht and his assistants, Wilhelm Groth, who later became a physical chemist, and also with Hans Gussmann. This name will be mentioned again at the very end of this biography (sect. 7).

Already since Davy and Berzelius, 'progressive' inorganic chemists had made several attempts to apply the chemical theory of valency, not only to systematize empirical findings, but also to search for physical clarification of valency strength. For ionic bonds Kossel^[21] as well as Born, Haber and Fajans^[22] had obtained lasting results, although the empirical parameters of their electrostatic theories needed further theoretical, calculable and physical foundations.

At the start of the studies of quantum chemistry, when such foundations were still far off, the Dutch scientists van Arkel and de Boer had undertaken a critical synopsis of the classical-electrostatic aspects of chemical interactions. The Hannoverian inorganic chemists Biltz, Klemm, Fischer used their treatise in a reworked German book version, for which Hellmann edited the sections on ionic size, crystal structure, atomic structure and the quantum mechanical description of covalent bonds.^[20]

2.4. The Early Days of Quantum Chemistry: Phenomenal Results! with Understanding?

During the three years from 1930 to 1932 Hellmann made himself thoroughly conversant with new developments in quantum mechanics, without, however, publishing anything himself. The advances at that time were regularly published in the form of review articles by London, Hund, Heitler, Born, Herzberg, Sidgwick^[23] and others. Three quantum mechanical procedures were then under discussion: i) The spin valence (SV) method of atomic term functions, as a *multi-electron Ansatz* for chemical bonding, which since 1927 was based on researches by Heitler, Rumer, Weyl (Göttingen) and London (Berlin);^[24] ii) its simplification and further development since 1931 by Slater (Chicago)^[25] and Pauling (Pasadena)^[26] in the form of the valence bond (VB) method of unhybridized or hybridized atomic orbitals, as an approach for *pairs of electrons*; and iii) the developments by Hund (Göttingen)^[27] and Slater^[28] and foremost Mulliken (both at Chicago)^[29] of the method of molecular orbitals (MO), with a *single electron starting point* as a description of valency. One of the centres of this turbulent development was Göttingen, situated only 100 km south of Hannover, where Hellmann also cultivated his contacts. The extensive series of articles by Mulliken, Slater and the linguistically gifted Pauling already pointed to the fact that leading centres of quantum chemistry were arising in the United States.

Another three aspects of the approach to quantum chemistry consisted of its procedural content: i) Heitler, Rumer, Weyl and Hund were exponents of *the formal-mathematical* advances of Göttingen, ii) the German physicists London and Herzberg and the two Americans Slater and Mulliken emphasized the

physical concepts, and iii) the latter, and later Hückel (Stuttgart) and Hellmann, and above all, Pauling advocated 'American' *pragmatism*^[6] and made good use of semi-empirical approaches.

Explanations for the already quite successful results of formal calculation of bond energy and molecular structure were only (though in parts eloquently formulated) references to “spin-coupling”, to “resonance of atomic states” and to “electron exchange within 10^{-10} s”^[8] (much too slow, this would correspond to 10^7 atomic time units, i.e. 10^{-6} eV of energy!). Or to the “drop” in potential energy, because “it *requires* a relatively small amount of *energy* to pull a certain amount of charge from the inner part of the atom, where it is ordinarily found [because the potential is low there], out into the region between the atoms [where the *potential is higher*]. It can very well be that *this decrease of potential energy* [logical inconsistency!] made possible by the change can *decrease* the total energy”.^[34] Unfortunately the mathematical-physical significance of such formulations is partly obscure, partly erroneous. It remains a psychological problem to clarify, how qualified scientists can arrive at these formulations. Nonetheless, in some individual cases, for instance ref. ^[24], it was conceded that real understanding was still a long way off.



Figure 3: A personal event occurred during the time at Hannover: on Hellmann's birthday in 1929 his son, Hans Hellmann junior, was born. The photo shows mother and son in the year 1930.

2.5. Working towards a Lectureship: the Semi-Empirical Calculation of Chemical Bonding

Against this background Hellmann decided to proceed in two different ways. On the one hand he made use of the available procedures without prejudice, with which he combined various new types of semi-empirical starting points and then obtained *semi-quantitative results* for concrete molecules. On the other hand he wanted to obtain not only a plausible explanation which appealed to common sense, but also a mathematically conceptual and clearly comprehensible analysis and explanation of the nature of the (more or less polar) covalency. In 1933 he published two important works in the “Zeitschrift für Physik” on those two subjects [H13, H14] and debated them at meetings of the German Physical Association in Hannover and Clausthal [H13a, H14a].

In his first work on the subject of “quantum mechanics of chemical valency” [H13] Hellmann broadened the conventional application of the SV theory through a semi-empirical approach, utilizing the already known properties of all diatomic fragments occurring in the molecule. Open discussions with the Hannoverian chemists had allayed the fears of the physicist Hellmann, who was conversant with the purely theoretical ideas of the University of Göttingen, and he was therefore motivated to introduce empirical facts into pure theory. The present method known as “Diatomics in Molecules” (DIM)^[31] was thus foreshadowed. Unfortunately the earlier work was forgotten in the light of later developments, possibly because of the fact, among others, that Hellmann had to go back to the complex Rumer diagrams of spin coupling in order to take account of the Pauli principle.

From the spectroscopic data of the diatomic fragments H_2 , NH and N_2 Hellmann obtained quantitative statements about the multi-atomic molecules NH_3 , NH_4 , N_2H_4 and N_3H . In the case of hydrazoic acid he was able to exclude the (then still debated) triangular form of the N_3 residue in favor of a linear structure. He also recognized the instability of the NH_4 radical. Furthermore he was able to roughly quantify the

binding energies of CH₄, C₂H₂, C₂H₄ and C₂H₆. He did, however, see the limitations of the method with respect to the outlying number of Rumer diagrams, which would have to be taken into consideration if it were required to deal with more general organic molecules.

The Molecular Virial (Hellmann-Slater) Theorem and Conclusions drawn therefrom

The Virial Theorem allows the kinetic energy T and the potential energy V to be uniquely determined, for a stationary system, if its total energy E is known. For a diatomic molecule with nuclear separation R it is:

$$\begin{aligned} T(R) &= -E(R) - R \, dE/dR \quad , \\ V(R) &= 2E(R) + R \, dE/dR \quad , \\ E(R) &= T(R) + V(R) \quad . \end{aligned} \tag{1}$$

For molecules at equilibrium separation $R = R_e$, as for the completely separated atoms, the force on the nuclei vanishes, $K = dE/dR = 0$. Then the positive kinetic energy with a changed sign is exactly equal to the negative total energy:

$$T = -E \quad \text{and} \quad V = 2E \quad . \tag{2}$$

This gives for the bonding energy ΔE , as the difference between the molecular and atomic energies, the following:

$$\Delta T = -\Delta E \quad \text{and} \quad \Delta V = 2 \Delta E \quad . \tag{3}$$

That is, in every stable molecule, independently of the bonding mechanism, the kinetic energy increases by exactly as much as the total energy of bond formation has decreased; i.e. by the bonding energy $\Delta E < 0$. In every case the main contribution to ΔE is made by the potential energy, which has decreased twice as much as the total energy. "Nature" reveals only *whether* a system has large, small or no bond energy, i.e. is bonded strongly, weakly or not at all. The question of the bonding mechanism asks, how human understanding can deduce, which physical situation must have occurred in each given case. The explanation and understanding of bonding phenomena therefore have an objective and a subjective aspect. The characteristic aspects of various bonding mechanisms (covalent, ionic, van der Waals etc.) can only be made evident by using "suitably tailored" approximation descriptions, which (a) reproduce the naturally occurring bond energy acceptably, and (b) describe the "essence" of the different types of bonding mechanisms.

With greater distances $R > R_e$, the potential energy curve increases, i.e. $dE/dR < 0$. Correspondingly $T(R)$ is then less than $-E$. For long-ranging Coulomb interaction, $E_c \sim -1/R$, the kinetic energy does not change with distance, $\Delta T = 0$! That is, the ionic bond energy is determined by the potential energy alone, $\Delta E = \Delta V$.

In the case of the van der Waals interaction the reduction in kinetic energy is by far dominant, independent of the type of interaction (be it dispersion or dipole or dipole-induced dipole). It overcompensates for the significant increase in potential energy:

$$\begin{aligned} \Delta E &= -C / R^6 \quad , \\ \Delta T &= -5C / R^6 \quad , \\ \Delta V &= +4C / R^6 \quad . \end{aligned} \tag{4}$$

When two open-shell-atoms approach each other and start to form a covalent bond, then at first the kinetic energy falls, while the potential energy increases only slightly.

In order to understand these partly paradoxical relations, it is necessary to devise 1) a simple physical model for the bonding mechanism concerned and 2) consider how such a simple description can be modified to obtain both, values for the stationary bond energy, and also reasonably correct values for the sensitive individual energy contributions.

2.6 The Two Fundamental Theorems of Hellmann on Chemical Bonding (1933)

A few months later he put forward what proved to be without doubt his most significant work "On the role of the kinetic electron energy for the interatomic forces" [H14]. To solve the molecular energy integrals over the atomic-orbital basis functions χ_A , it had become customary from the beginning of quantum chemistry to replace the kinetic energy term ($-1/2 \nabla^2 \chi_A$), according to the atomic Schrödinger equation, by $(E_A - V_A) \cdot \chi_A$, where E_A is the total energy and V_A the potential energy in atom A. Through this trick the kinetic energy had been eliminated from both the VB and MO expressions of the chemical bond energy: Now the bond energy consisted only of potential energy terms of one and two electron type. A discussion of the physical nature of chemical bonding should, however, take into consideration the interplay of all four energy terms: nucleus-electron attraction; nucleus-nucleus repulsion; electron-electron repulsion; and kinetic electron energy. Of these, only the first term is negative, i.e. stabilizing.

Thus some of Hellmann's colleagues arrived at the "immediately plausible" argument, that only the potential energy, and particularly that of the nucleus-electron attraction, could be the physical cause for a stable bond. This argument has been retained over decades as: "the existence of chemical bonds must be attributed to the first [i.e. the electronic-nuclear potential] term; it is the only term in the energy expression corresponding to attractions. – bond formation ... can arise only from attraction between the positive nuclei and a growing negative charge in the bond region"^[32, p.71] (compare also ^[34] and ^[32]). The fact that bonding can be due to a *relative* reduction of destabilizing energy contributions was accepted by a few people only, at the time, and even nowadays causes problems to some.

Hellmann now succeeded in averting the danger of pseudo arguments. Parallel to each other he discussed the clearly explicable physically motivated approaches, and the totally different divisions into kinetic and potential parts of the exact total energy values. He derived two theorems on this, and with their help he worked out the variations of energies as a function of internuclear distance R [H14, H14a]. These two "Hellmann theorems" are represented, in modern parlance, in the two *info-boxes* on pages 6 and 8.

The *Molecular Virial Theorem*, which Hellmann obtained in July 1933 from a formula by Fock,^[33] is often quoted in conjunction with a slightly later, very clear work by Slater of August 1933.^[34] We may therefore call it the *Hellmann-Slater Theorem*. – When the *Hellmann-Feynman Theorem* (i.e. the *Molecular Force Theorem*) was cited in earlier literature after the Second World War, it was based on Feynmann's work of 1939^[35] and only later on Hellmann's book [H33, H34], though not on the original Russian version finished October 1936 [H33, see p.428], but on the slightly abridged and revised German version finished March 1937 [H34, see p. 285f], which had been lithographically reproduced in the USA during the Second World War in 1944. The formal relationship (5) (see *info-box* below), without the specific utilization and application (6), can already be found within the framework of perturbation theory of Schrödinger (1926) and Pauli (1933).^[36]



Figure 4 : Hellmann in pensive conversation with his sister, Greta Munkelt, around 1930

2.7. On the Nature of Chemical Bonding: Clearly Comprehensible and Mathematically Correct

In addition to his extremely careful formal discussion, Hellmann took great trouble to work out basics, such as the details of chemical bonding, and to "establish a clear understanding of the theory by the simplest possible means" [H16]. First of all he pointed out that electrons, which were restricted in a special region of Δx , were confined by the uncertainty relation $\Delta x \cdot \Delta p \geq h/4\pi$ [h being Planck's constant] and were, therefore, compelled to accept a minimal amount of kinetic energy of more than $(\Delta p)^2/2m$, even in the energetically most favorable zero-point state. This zero-point effect was solely responsible for all the »non-classical«, » non-concrete« effects. In combination with the Pauli principle this afforded Hellmann a quantum-mechanically correct interpretation of chemical bonding.

The lower the energy barrier between a pair of atoms, the more extended the orbital of an electron about them will be, and the higher will be the corresponding tunneling frequency. Hellmann carefully distinguished between the tunneling frequencies ν_A of atomic states when they lose their steady state character through overlapping, and the bond energy BE_M of steady state molecules, for which the relation $BE_M = h\nu_A$ holds. He thereby removed the mystical element from the concept of electron exchange and gave it an explicable inherent meaning. In this way he explained that covalent bonding is a typical single-electron effect. He established the "kinetic energy pressure" reduction of molecular quantum mechanics

as a consequence of the Uncertainty Principle. He further explained the frequent appearance – only slightly impeded by electron-electron repulsion – of pair-bonding of electrons as a consequence of the Pauli principle. He also explained, as did Pauling, how it is just the electron-electron repulsion that favors pair-bonding in hetero-nuclear systems, whilst a single electron bond quickly loses strength for increasing electronegativity difference, to use Pauling's concept. Hellmann also analyzed dispersion interactions with respect to kinetic and potential energy contributions with "surprising results" (see *info-box* above on *The Virial Theorem*).

In particular Hellmann concerned himself with making the non-concrete aspects of quantum mechanics clear with the help of semi-classical statistical descriptions. If two atoms approach each other and their individual phase-space cells (today we may say their atomic orbitals) are occupied by single electrons only, then if their spin directions are opposed, their electron clouds can expand into the space of the neighboring orbitals, leading to a reduction of kinetic and total energy, which then results in chemical bonding. If, however, atoms with the orbitals occupied by two electrons each, approach then the above mentioned delocalization is not possible because of the Pauli principle, and the resulting compression in configuration space leads to an increase in kinetic and total energy and thus to 'closed-shell closed-shell' repulsion.

2.8 Further Work on Chemical Bonding

Although Hellmann was assistant to Prof. Fues who occupied the chair of theoretical physics & applied mathematics, he kept in touch with Professors Precht and Herweg of the institute of experimental physics and high-frequency technology, where he and his student Röver received experimental support for renewed research into electrolytic solutions (see sect. 1.2) - and this was at the local veterinary college (see below sect. 2.9).

He further shared his interest in the nature of chemical bonding with Professor Braune's assistant from the department of physical chemistry, the lecturer Jost, who had qualified in 1929. Intensive discussions led to the two works in "Zeitschrift für Elektrochemie" [H16, HC16] "On understanding the 'chemical forces' through quantum mechanics" which were addressed "to a wider circle of chemists". Part I [H16] was not ready until the autumn of 1934 when Hellmann had been forced already to leave Germany. The second part was completed in 1935 by taking into account Hellmann's latest results from Moscow [H17-H20] as well as the newer works of Pauling, Wheland, Slater, Mulliken, Hückel, van Vleck, Eyring, Gombás, Polanyi, Ingold, among others, with the final preparation by Jost alone [HC16].

The basic contributions to quantum chemistry so far mentioned, and probably further ones (for instance pseudopotentials on the basis of density functionals, [H17]) were summarized in a monograph i.e. a manuscript which can no longer be traced. This, too, was thoroughly discussed with Jost and later typed by Mrs. Jost. This was to form the basis for the first chapters of his book "Quantum Chemistry" [H33, H34]. Whether the manuscript had anything to do with the inaugural habilitation dissertation is not clear. In Hannover, and not only there, many documents from the Nazi period seem to have been lost towards and after the end of the Second World War. Many related documents in Berlin ministries had already fallen victim to the bombardments during the war.

Hellmann expanded his theories on interatomic forces from his foundational work of 1933, but was not able to write this up until the summer of 1934 in Moscow [H18]. That the really clear ideas were then rarely assessed is explained in a paper published by Hellmann in 1936 [H26]. He pointed out that Hill as well as Bridgman had not correctly understood the meaning of the Virial Theorem and the consequential partitioning of the bonding energies into their kinetic and potential parts. Although Hellmann's ideas were deeply extended by Ruedenberg and published in English in 1962^[37] and were reported, for instance, by Kutzelnigg^[38] or Mulliken^[39] with clarity and profound understanding, Hellmann's criticism is unfortunately still valid today with respect to many textbooks dealing with chemical bonding. Such intellectual misunderstandings had impressed Hellmann to the extent that he even mentioned these discussions in a letter to his mother. It is also notable that Hellmann's ideas, although often quoted, are usually referred to in an extremely abbreviated form. Kutzelnigg is right when he points out how grotesque this situation was (see^[38], especially pages 556/7 and quote No. 17).

The Hellmann-Feynman (Molecular Force) Theorem

The Hellmann-Feynman Theorem describes the force between two nuclei of a molecule

$$dE/dR = \langle \Psi | \partial H / \partial R | \Psi \rangle \quad (5)$$

$$= Z_1 Z_2 / R^2 - \int dr^3 k(r) \rho(r) \quad (6)$$

Here Ψ is the electronic wave-function of the molecule and H the Born-Oppenheimer Hamiltonian operator. Z_1 and Z_2 are the two nuclear charges, $Z_1 Z_2 / R^2$ is the Coulomb repulsion force between the nuclei. $\rho(r)$ is the electron density distribution in the molecule and $k(r)$ the force of attraction between a selected nucleus and an electron at position r .

That is, the force between two atoms derived from the total quantum-mechanical energy can thus be obtained using strictly classical electrostatics as the Coulomb force of the selected nucleus on the electronic charge cloud and the other nucleus; provided the electron density $\rho(r)$ is known exactly! The theorem makes two points. Firstly that with a nuclear shift (e.g. vibration) the alterations in kinetic electron energy and electron-electron repulsion are exactly compensated for by the remaining relaxation energy corrections of the electron cloud; and secondly that the force integral is numerically extremely sensitive to small errors in $\rho(r)$, which greatly limits the practical applicability of the theorem.

2.9. Physics Lectureship at the Veterinary College and Dismissal by the National Socialists

Scientific education at the veterinary college Hannover (Tierärztliche Hochschule = TiHo), was one of the best in Germany and was partly in the care of staff members of the Institute of Technology (Technische Hochschule = TH). When the lectureship in physics at the TiHo, which had only moderate financial and experimental remedies, fell vacant in the autumn of 1931, Hans Hellmann obtained this post, since, according to Professor Fues, he was likely to qualify. On the basis of the two works mentioned above in quantum chemistry, Hellmann handed in his 'Habilitation' dissertation in 1933.

In the meantime Hitler had become Reich Chancellor on 30th January 1933. This was followed by public, political and social life being "brought into line". After the National Socialist German Workers' Party (NSDAP) seized power, they created new laws on the one hand, and on the other the SA and SS caused public riots against communists or social democrats and increasingly against Jews. Hans Hellmann was to experience both.^[40]

The students at the TiHo were extremely enthusiastic in 1933 about the National Socialists coming to power.^[40] Hellmann, who was regarded as not "politically correct" (which meant at that time, because of his leftist tendencies) had to put up with abuse being shouted at him by the students from the very beginning. On the 10th of May the Hellmann family were eye-witnesses to a book-burning. They became so insecure in these circumstances, that they destroyed part of their home library, which, besides classical socialist authors also contained belletristic works by Heine, Fallada, Ringelnatz, Zweig, Tucholsky, and the weekly "Weltbühne" for politics, art and economics, also prohibited by the Nazis. The National Socialist "law for re-establishment of civil service professions" dated 7th April at first only questioned applicants as to their "Aryan" origins and this did not affect Hellmann. (Teachers, lecturers etc. at state schools and universities in Germany were [and are] "civil servants"). This changed, however, with the Reich Law of 30th June: when applying to submit his dissertation, Hellmann had to give details of his wife's racial origin. As a result the Prussian Ministry of Culture refused permission in the autumn of 1933. On 24th December 1933 he received his notice with effect from 31st March 1934, since he could no longer hope to qualify because of his wife's non-Aryan origin.^[40] Working directly together with his student Röver or with his assistant colleague Jost (see sect. 1.2 [H15, HC15], and sect. 2.8 [H16, HC16], respectively) was no longer possible. His "doctoral father", Prof. Regener, was dismissed by the Nazis 'only' in 1938, despite his tenure.

For Hellmann, as for many of his colleagues, for instance those famous ones from Göttingen, there remained only emigration. Further work on quantum chemistry in Germany was drastically curtailed. Hellmann had built up contacts both to Eastern Europe and to America. At that time he obtained a third offer from an institute in the Soviet Union, he also obtained an offer from the USA. In the question of "East or West", Hellmann fatally decided, for various reasons, to go to the Soviet Union.^[95]

3. Hellmann's Publications

Hellmann's works all of them as far as they have become known to us, are listed at the end of this article in an *Appendix*. They are arranged (mainly) chronologically according to the date of receipt of the manuscripts (given in parentheses).

References with "H" in front of the running number have Hellmann himself as main author or co-author.

References with "HC" followed by the number refer to work by Hellmann in co-operation with colleagues and co-workers, where the fact that Hellmann was a co-author was not or could no longer be mentioned in the German Reich or in the Soviet Union for political reasons.

Names printed in cyrillics were transliterated according to the rules given in the Register of Authors of Chemical Abstracts, with slight variations: "i kratkoje" = j, ë = jo. The languages of the articles are indicated by letters (D = German, E = English, R = Russian).

A lower case *d* indicates the availability of a German translation in the Hellmann-Archive. Original issues of reprints and books available in the Hellmann-Archive are indicated by a fat letter **O**, otherwise copies exist.

Hans G.A. Hellmann (1903 - 1938)¹⁾

Part II. A German Pioneer of Quantum Chemistry in Moscow

By W.H.E. Schwarz^{***}, A. Karachalios^{e)}, S.R. Arnold^{b)} and
L. Zülicke^{h)}, P.C. Schmidt^{g)}, M.A. Kovner^{f)}, J. Hinze^{a)}, H Hellmann jr.^{d)}, J.Heidberg^{c)}, D. Andrae^{a)}

*The protest of "natural common sense" has probably been felt
at every important step taken during the progress of natural sciences,
and science has nevertheless stepped across this protest
under the inescapable pressure of facts [....]
Quantum chemistry does not claim any more than
all chemical and physical material properties
to be capable of purely theoretical precalculation,
simply on the basis of one single mathematical law [...and]
of creating a theoretical reconstruction of the chemical world.*

Hans Hellmann, 1936 [H30]

In the first part we told of Hans Hellmann's studies of physics in Stuttgart from 1922 to 1929 with Ointermediate 'stops' in Kiel and Berlin, and of his time as a lecturer from 1929 to 1934 in Hannover. After the National Socialists took power, emigration became his only choice, chiefly because of his wife's Ukrainian/Jewish origin.

4. An Emigré in Russia (1934-1938)

4.1. The Search for a Postdoctoral Position

As an ambitious scientist, Hellmann obviously had been interested in contacts abroad. It is understandable that, partly because of his wife's Ukrainian origin and partly because of his own affinity with socialist ideas, Hellmann was especially interested in a postdoctoral position in the Soviet Union, particularly in the Ukraine. He also had contacts to the USA (Boston), although this is not well documented in detail.^[94] The Soviet Union had become attractive to natural scientists, since in the 1920s it had quickly reached scientific world level through intensive state furtherance of technology and the natural sciences.^[41,42] It was therefore not unusual to see exchanges of scientists between 'western countries' including Germany and the Soviet Union in the 1920s and early 1930s.

Through the mediation of Victor F. Weisskopf, then still at Göttingen, Hellmann received an invitation in 1931 from Alexander Weissberg, the director of the Ukrainian Physical Technical Institute in Khar'kov, the Ukrainian capital at the time. This institute had been founded in 1929 on the initiative of Abraham F. Joffe. It had rapidly developed into one of the leading physical research stations in the Soviet Union, with such well-known scientists as Lev D. Landau, Lev V. Shubnikov, Friedrich G. Houtermans and Alexander Weissberg, who kept up lively international contacts. Paul A.M. Dirac, Boris Podolski, Rudolf Peierls und Victor Weisskopf were among the temporary guests.^[42]

Hellmann received a further invitation, also through Weisskopf, from Dnepropetrovsk, a city with over one million inhabitants between Kiev and the Black Sea, which also had a similarly strongly supported physical university research institute. This was the realm of Boris N. Finkelstein, another scientist of the Göttingen group, who had published an important work on H_2^+ ^[43] and, like Hellmann, was interested in questions of both quantum chemistry and electrolytes. Hellmann was unable to take up either of these invitations, since the Soviet authorities in both cases refused him a visa.

Lothar W. Nordheim, who was then still at Göttingen, had established contacts already in 1932 with the Karpov Institute in Moscow, a leading centre of physical chemistry in the Soviet Union. Yuri B. Rumer, who at Göttingen had made essential contributions to the theory of spin-valency ('SV', see part I, sect. 2.4) was again working in Moscow. (At those times the preparations for a war had already started, and all scientists working abroad were called back to the Soviet Union.)^[41] Rumer, as also the physicist Hortheimer, who had emigrated to Paris, supported Hellmann's application, so that he was offered an attractive position by Director Bach of the Karpov Institute, whose deputy Hellmann had already been

¹⁾ See footnotes on page 1

able to meet in the summer of 1933 in Berlin. Thus Hellmann managed to escape the political pressure in Germany (see sect. 2.9) when he finally received both exit and entry visas for himself and his family. At the end of April 1934 they removed to the Soviet capital on board the Berlin-Moscow-Express, when again Yuri Rumer was most helpful.^[44] The search for a new realm of scientific experience had turned into the forced emigration of the Hellmanns.



Figure 5: Hans Hellmann in the 1930s

4.2. The Karpov Institute

The Karpov Institute was named after the first leader of the Soviet chemical industry, Lev Yakovlevich Karpov, and this research centre enjoyed political support, since its investigations were considered militarily and economically significant. It had been founded on the 4th October 1918 as a central chemical laboratory, and since 1932 it came under the aegis of the People's Commissar of Heavy Industries, Grigorij K. Ordzhonikidze. The board of the Karpov Institute consisted of two members of the Academy, the biochemist Aleksej N. Bach, and the surface scientist Aleksandr N. Frumkin. 150 scientists were employed at the Institute in 1934, including several foreigners, plus 250 non-scientific co-workers. The Institute's eight different departments had the task of research in basic physical chemistry as well as the application of research results to the solution of problems in industry, and armaments.^[45,46]

It soon became the leading institute of Physical Chemistry of the Soviet Union. Most work-groups there had well founded physical-mathematical background knowledge and were open to theoretical concepts. Quantum chemistry was accepted as an integral part of their science by those physical chemists, as an enrichment of their arsenal of methods, and as an independent subbranch of science. In Germany, where quantum chemistry had been brought to life by physicists with the help of rather complex methods (especially spin valence theory, SV),^[7,24] this field was not wellcomed very much by the *ordinary* chemists' community. The same happened in Russia according to the motto: organic and inorganic chemistry are engaged in organic and inorganic substances, which substances are the topic of theoretical chemistry? Purely theoretical substances? Does quantum theory have any useful role in chemistry at all?^[96]

In the "department of the structure of matter" of the Karpov-Institute, under the leadership of Ya.K. Syrkin, who later wrote a well-known textbook on quantum chemistry^[47] Hellmann started his job at the beginning of May 1934 as "head of the theory group". The staff records of the Karpov Institute show Hellmann as an "expert in theoretical physics and theoretical chemistry". There was another theoretical group in the same department whose head was party member A.A. Zhukhovitskij, who later 'criticized' Hellmann (see sect. 7) and who was later quickly promoted in his career as assistant director of the Karpov Institute. Apart from the two "theory groups" this department had three further groups, with an experimental orientation: 1. one for dipole moments and associated systems, headed by Ya.K. Syrkin himself; 2. one for dielectric constants under V.G. Vasil'yev; and 3. one for the Smekal-Raman-Effect headed by M.V. Vol'kenshtein. The Raman effect had been proved experimentally in 1927, nearly simultaneously in India, in France, and in Russia, where it was called combinational light scattering.

Hellmann had close contacts with many departmental colleagues. He maintained friendly contacts also with scientifically highly regarded colleagues from other departments of the Karpov Institute: besides his principal Syrkin working on kinetics and catalysis - with Tjomkin (Temkin), the leader at of the department of Theory of Adsorption and Catalysis, a physical chemist of broad scientific interests and knowledge; with the electrochemist Frumkin, leader of the department of Surface Phenomena; and with the organic chemist Njesmjejanov. Hellmann also communicated with colleagues and friends from the famous Leningrad Polytechnical Institute (Y.I. Frenkel, V.A. Fock),^[42] with Dr. Novikov from Moscow, working on mathematical logic and applied mathematics, and with others.

4.3. Personal Career

In the course of the following three and a half years Hellmann supervised a series of co-workers – master and doctoral students and postdoctoral fellows - such as V. Kassatochkin [H27, H28], K. Majeveski [H36, HC36], M. Mamotenko [H37, H39, H40, HC44], N.D. Sokolov [HC41], S.J. Pshezhetskij [HC42] and M.A. Kovner [HC43]. The Hellmann archives contain the copy of a photograph showing departmental members in conversation during a seminar. Among them was M. Mamotenko who was reported missing during the war. The others had more or less brilliant scientific careers in the fields of theoretical and physical chemistry.

Hellmann's new post, compared with that in Hannover, was a distinct improvement. As a natural scientist he belonged to a profession which was highly regarded in Soviet society. Many new natural science institutes were opened and allocated generous budgets.^[41,42] Up to the mid-thirties, scientists, particularly from abroad, were provided with apartments, jobs and received assistance with everyday needs to a far greater extent than the rest of the population.^[44] In return, however, the system demanded a high degree of loyalty.

After the moderate possibilities for this qualified experimental and theoretical physicist and physical chemist at the TiHo Veterinary College in Hannover, and after the oppressive experiences with National Socialism and the economic crisis in Germany, Hellmann enjoyed life in an "exotic" country as well as the advantages which came with his new status.^[44] Even in his first year he traveled to two international conferences in Kharkov and Leningrad, where he met scientists from all over the world, among others Niels Bohr, Paul A.M. Dirac and Jean-Baptiste Perrin. "There is quite a difference", he wrote to Germany in August 1934, "between sitting isolated in some provincial place, and working at an Institute together with the scientific elite from a people of 150 million. This is where I have the scientific contacts I need." In spite of some difficulties at the Russian and German consulates, he managed to obtain a visitor's visa for his mother in 1935. After being urged by the authorities to apply, Hellmann received Soviet citizenship on 16th June 1935 and celebrated the event with colleagues at home in his apartment. This would later prove to have contributed to his ultimate fate (see sect. 7).

Hellmann's success at the Karpov Institute was remarkable.^[46] at the beginning of 1935 he was granted a "doctorate", the Russian qualification for lectureship, which he had been denied in Germany because of his wife's Jewish descent. In the same year he took part in a conference in Dnepropetrovsk, where he was elected to the organizing committee for a 1936 conference on quantum chemistry. The Institute repeatedly gave him special prizes for "extension work"^[48] or "research which led to important new results". In November 1936 his starting salary of 700 roubles was increased to 1200. In December 1936 he was invited to address the Academy of Sciences [H*]. It may be that he was to be considered as a possible Candidate, but his knowledge of Russian was still inadequate.

During the years in Moscow he published scientific papers approximately every two months. His success brought him further academic honours: On 1st January 1937 he was made a "full member" of the Karpov Institute (a title corresponding to that of a professor at a university) and at the beginning of his last year of life (autumn 1937) he was declared a "Leading Scientist".

5. Scientific Successes

5.1 Development of the Pseudopotential Method: Atomic Core Potentials

Having arrived in Moscow in early summer 1934, Hellmann immediately began to publish a series of articles [H17, H19, H20, H25, H27, H28, H29], the start of the solutions to two basic problem areas concerning the mathematical-physical descriptions of chemical phenomena. For one thing, the atomic number N of chemical elements covered two orders of magnitude. Since *the cost* of quantum-chemical treatment of such systems increases with some power of N , the practical chemist has access only to ridiculously small systems for theoretical reconstruction or precalculation.

Furthermore, the periodic table of elements is the most important classification system in chemistry, where qualitatively similar types of elements are grouped together whilst their atomic numbers drastically differ from each other. The Schrödinger equation, whose ab-initio quantum chemistry includes the electron number N , does not, initially, clarify *the affinity relations* between the elements of the vertical columns of the periodic table. Hellmann had formulated [H30]: "A purely theoretical derivation of properties of materials always means returning from quality to quantity".

A way out of both problems would be if one could confine oneself to calculations regarding the valency electrons only. How then, can the role of the core electrons be described in a simple way?

Orbital Model

Orbitals. The work horse of quantum chemistry is the Orbital Model (i.e. the Hartree-Fock (HF) method and the Kohn-Sham (KS) density functional approach). Orbitals describe single electrons in the Coulomb field of the nuclei and in the average HF or KS repulsion field of interacting electrons. As this field differs drastically from that of a point charge, the virial theorem for HF and KS valency orbitals also differs from the respective energy relation of a system with point charges,

$$T = -V/2 = -E \quad (7)$$

For those orbitals, there holds qualitatively:

$$T_{\text{orb}} \sim -V_{\text{orb}} \gg -E_{\text{orb}} \quad (8)$$

where V_{orb} , T_{orb} and E_{orb} are respectively the potential, kinetic and total energy of the orbital.^[50]

Different sets of Orbitals. As all electrons of a system are experimentally indistinguishable, the partitioning of the measurable total electron density into contributions of orbital densities of single electrons or electron pairs is more or less arbitrary. Common sense as well as didactics have problems with this situation, which however offers the unique advantage to prepare orbitals which in each case are specially suited for a simple description and explanation of the underlying problem. A further advantage of the orbital model is that we can obtain easily interpretable semi-classical and rather simple formulas for energy and other observables **if** the orbital set is chosen to be orthogonal:

$$\int \mathcal{d}\mathbf{r}^3 \cdot f_i^*(\vec{r}) \cdot f_j(\vec{r}) = d_{ij} \quad (9)$$

where d_{ij} is the Kronecker symbol ($d_{ij} = 0$ for $i \neq j$). Different orbital sets describe exactly the same physical situation through different equivalent theoretical pictures.

Delocalized and Localized Orbitals. There are still many possibilities even for the choice of orthogonal orbital sets. *Canonically* chosen orbital sets satisfy especially simple equations; amongst other things they are delocalized over the molecule; they allow a simple description, for example, of VIS and UV spectra or photoelectron spectra, of concerted rearrangement reactions etc.. Orbital sets, which are chosen as *localized*, are recommendable for the discussion of atomic inner shell spectra (X-ray spectra), of local substitution reactions, of the quantum chemical interpretation of Lewis formulas, of the concept of valence-inactive atomic core shells, and for the foundation of additivity schemes of transferable electronic shells.^[57]

Pauli Repulsion. In the picture of orthogonal orbitals it turns out that the higher energy orbitals (for instance valency orbitals) always develop 'waves' in the spatial region of the n lower occupied ones, that is maxima, minima and zero points, corresponding in number to n . According to the quantum-mechanical formula for the kinetic energy of the electrons

$$T_{\text{orb}} = -1/2 \int \mathcal{d}\mathbf{r}^3 \cdot f_i^*(\vec{r}) \cdot \nabla^2 f_i(\vec{r}) = +1/2 \int \mathcal{d}\mathbf{r}^3 \cdot | \nabla f_i(\vec{r}) |^2 \quad (10)$$

the strong curvature of the 'wave function' (f_i) or the squared steepness of the heavily oscillating wave function (f_i^2) in integral (10) yield the large value of the kinetic orbital energy noted in eq. (8) for valence electrons penetrating into regions occupied by the atomic core electrons of same spin. The respective increase of energy upon overlap of occupied orbital shells is known under the headline "Pauli repulsion" [H16].

Pauli-Repulsion

When atoms approach each other, the outer valency electrons penetrate the occupied shells of another atom where they are no longer completely shielded from electrostatic nuclear attraction. Through his concern with the essence of chemical bonding (see part I, sects. 2.7 and 2.8) Hellmann had, presumably while still at Hannover, recognized that "the coupling of single electrons by the Pauli principle was just as important as their electrostatic interactions" [H34].

The best way of obtaining a physical understanding of this coupling is to look at it within the framework of the orbital approximation, see the corresponding *info-box* below. Thus the Pauli principle causes a

repulsive action of the occupied atomic shells, through the increase of the kinetic energy density of the penetrating valency electrons. Hellmann described this effect soon after his arrival in Moscow in June 1934 in a short paper [H17] in both German and Russian, by means of an "additional potential", which is now called a "pseudopotential" (see respective *info-box* below). The additional potential compensates for the powerful nuclear attraction in the interior of the atomic core, as Hellmann sketched in *Fig. 6*. So the valency electrons do not collapse into the atomic centre [H20, H34]. Hellmann established the "additional potential" with the help of the Thomas-Fermi density functional approach for atoms [H29],^[52] but then he used a simple function for the additional potential, which was semi-empirically adapted to experimental atomic energies, thus allowing for compensation of errors.

Pseudopotentials

In atoms, molecules and crystals, chemists tell us, the chemically *active valency* electrons move around in the fields of rather inert atomic nuclei. The *valency electrons* feel the attractive electrostatic nuclear Coulomb charges, which are somewhat shielded by electron-electron repulsion of the other electrons' density. In addition to this attractive "Hartree" potential there is the exchange correction (Hartree-Fock potential) and the correlation or polarization correction (Kohn-Sham potential): $-V_{\text{attr}}$.

In the orthogonal orbital model, (see *info-box*) the *valency orbitals* now have to be supplied with pronounced oscillations in the region where the atomic core electrons remain. This requires a high numerical effort, e.g. many core-type basis functions for the valency electrons which are mainly found outside the core.

The result of the Pauli-principle is a relative increase of kinetic energy of the valency orbitals, T_{orb} , ("*kinetic energy pressure*" according to Hellmann), when the valency orbitals overlap with occupied atomic cores, which can be simulated by a potential which is repulsive in the core regions. Hellmann called it "additional" potential ("Zusatzpotential") [H20] :

$$+V_{\text{add}} = ?T_{\text{orb}}/?? \quad , \quad (11)$$

Inside the atomic cores the attractive $-V_{\text{attr}}$ is largely compensated by the repulsive additional potential $+V_{\text{add}}$. A sketch of the total, so-called effective potential

$$V_{\text{eff}} = -V_{\text{attr}} + V_{\text{add}} \quad , \quad (12)$$

for the case of a caesium atomic core, Cs^+ , in a very simple approximation (i.e. a soft core potential) is reproduced in *Fig. 6* [H34]. Already Hellmann noted that the additional potential is angular momentum dependent, in principle.

Today V_{attr} and V_{eff} are called *pseudopotential* (PP) or *effective core potential* (ECP). They are represented by functions whose parameters are either determined by, or fitted to, quantum chemically calculated energies (and wave functions) or to experimental energies of suitable *atomic* states.^[53] It has turned out that the outer regions of the atomic core assist the valency action. Accordingly, the quantum chemist should count the outer atomic core shells ('semicore') and respective electrons among the valence set, i.e. $3s^2 3p^6 4s$ in the case of potassium, or $3s^2 3p^6 3d^6 4s^2$ in the case of iron.

The atomic effective core potentials are then taken over for calculations of *molecules and crystals*, where only the valency electrons need to be dealt with. The valency orbitals in the effective potential are called *pseudo-orbitals*. They approximate closely to the ordinary all-electron valency orbitals, however average out the oscillations in the spatial regions of the atomic cores. The pseudo-orbitals are relatively smooth and easy to represent.

Quantum-mechanically, all elements of one group of the periodic table are then represented by similar effective potentials (see *Fig. 7*) with the same number of valency electrons housed in similar pseudo-orbitals. In this manner the basic chemical experience, represented by the periodic table, is carried over into the basic physical equations. In the pseudopotential scheme the considerable kinetic energy of the valency electrons in the region of the atomic core near the nucleus is represented as the 'additional' potential energy. Hence the kinetic energy becomes less strongly positive and the potential energy less strongly negative. Qualitatively, the Virial Theorem for pseudo-orbitals gives in general

$$T_{\text{Ps}} < -V_{\text{Ps}}/2 < -E_{\text{Ps}} \quad (13)$$

(compare eqs. (7) and (8) with eq. (13)).

The Combined Approximation Procedure

Hellmann treated the valency electrons quantum mechanically in the effective field of the nucleus. He called the method the "Combined Perturbation Procedure". He briefly communicated the first applications regarding molecules K_2 and KH in an American journal [H19] at the end of 1934. In later more detailed

publications [H20, H25] he used the name "Combined Approximation Procedure" ("Kombiniertes Näherungsverfahren") [H27] which can be found in the literature, together with other similar names, up to the end of the 1960's (e.g. see [54,57]). Together with his co-worker Kassatochkin he subsequently dealt with the alkali and earth-alkali metals and could already then calculate the lattice constants to an accuracy of 3%, the cohesion energies and work functions to 25%, and the compressibilities at least semiquantitatively [H27, H28, H29].

Hellmann's Approximation Procedure achieved two objectives: i) Instead of taking into account all electrons, only the much smaller number of valency electrons needed to be treated quantum-mechanically. In addition, the 'smooth' pseudo-orbitals were easier to describe than the 'normal' valency orbitals with their core oscillations. ii) The other objective was that atoms and compounds from one group of the periodic table were represented by the same type of Hamiltonian with an equal number of valency electrons and only slightly differing pseudopotentials (see Fig. 7). Thus it becomes possible to link more or less steady trends in chemical properties with corresponding changes in pseudopotentials or effective core potentials.

As is so often the case with new scientific developments, there was some duplication here, too. Less than one year after Hellmann, in March 1935,^[55] Paul Gombás in Budapest also published the idea of modelling the core electrons statistically as an electron gas cloud and to simulate their action on the valency electrons through what he called "Pauli Occupation Exclusion Potentials" ("Pauli-Besetzungsverbot-Potentiale").

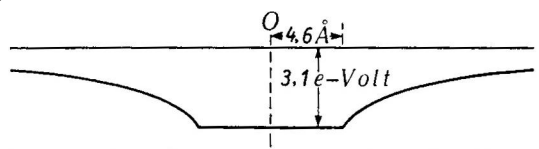


Figure 6: The effective potential of the combined approximation procedure for the Cesium atom [H34, S.39]

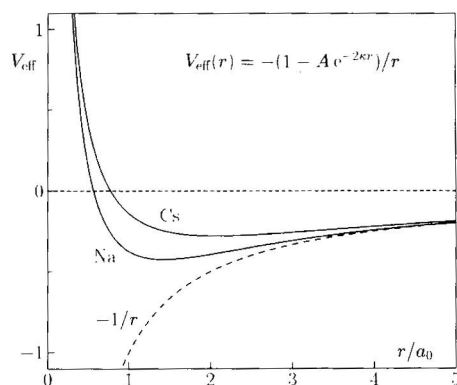


Figure 7: Effective core potentials $V_{\text{eff}}(r)$ in atomic units for sodium ($A = 1.826$; $k = 0.533$) and cesium atoms ($A = 1.672$; $k = 0.333$), as introduced by Hellmann and Kassatochkin [H28, Table 1] for the investigation of metallic bonding of the alkali metals. The determination of parameters A and k follows from fitting the energies of the single-valency electron atoms to the lowest experimental term energies. The approach was 'reinvented' since, begin with 1959.^[56]

Further Developments

Further developments in the pseudopotential method were slow at first, and followed different paths in molecular and in solid-state sciences. Initially many details had to be re-discovered (e.g. ^[56]), and older techniques had to be re-instated, before the pseudopotential procedure could be implemented as a standard, numerical, quantum-mechanical method for molecules and crystals in commercial programs. Essential in this connection was the slowly emerging understanding that pseudopotentials were angular momentum dependent operators. Even this insight seems to have been apparent to Hellmann from the beginning [H25].

One objective of the pseudopotential method was to perform calculations regarding whole groups of the periodic table, including the heavy elements. In those cases the angular momentum should mean total angular momentum, and spin-orbit coupling had to be taken into account together with other relativistic effects [H30, H33]. But Hellmann, just as Dirac, was unable to imagine this,^[58] although Hellmann

mentioned explicitly that the valence electrons are extremely fast when they penetrate into the atomic cores [H14]. This aspect in the field of pseudopotentials was clarified only in the 1970's.^[59]

5.2 Polarizabilities, Dispersion Forces, Electron Affinities

As in his early experiments, Hellmann also took the trouble in his theoretical researches to make precise analyses of all possible sources of error. He sought, through careful mathematical inquiry into simple systems, to determine "the limits of practical applicability of the common approximations", in order to arrive at "general points of view for later quantitative improvement" on questions of concrete details. This is typified in his works on non-covalent bonds: London's dispersion forces and classical ionic and polarization interactions [H21, H31, H32, H36, H38].

The dispersion formulas known at the time due to London, to Slater, and to Kirkwood,^[60] gave numerical values which in parts varied drastically. After a physically clear analysis of "the electrons' orbiting in time in different molecules", he warned against applying the approximation of the averaged energy denominator, and he suggested that individual shells should be summed up within the framework of the orbital model [H21]. He also pointed out that multipole expansions become invalid for overlapping charge clouds. For shorter distances he correctly calculated the dispersion energies significantly smaller than to be expected according to the asymptotic $-C/R^6$ -term [H36], while Pauling^[61] obtained the $+1/R^8$ -term with wrong sign, i.e. even greater dispersion energies for short distances. Hellmann's estimates of dispersion energies explained, for example, the preference to the cesium chloride structure versus the rock salt structure in the case of CsCl [H31].

Hellmann also established the obtuse bond angle of H₂O molecules with the help of covalent contributions to the ionic model, extended to include polarization contributions [H32, H38]. Similarly he obtained the high solvation energy of the Ag⁺ ion (with radius between those of Na⁺ and K⁺)^[62] in agreement with today's concept of the Ag⁺ as a soft, covalently interacting electrophile.^[63] Concerning the concepts of electronegativity and atomic valence states, Hellmann could, by exploiting his pseudopotential idea, markedly improve on the semi-empirical extrapolation formulas for electron affinities at that time [H37, H39, H40] (cf. ^[64]).

Further work done by his co-workers [HC41, HC42, HC43] on polar molecules, hybridization and the inversion barrier of NH₃ and on the Thomas-Fermi density functional approach did not appear until after Hellmann's sudden arrest without any mention of its initiator. Mentioning his name was obviously no longer convenient for the publishers of the magazines or the Institute submitting the articles. The last work under Hellmann's name is dated 11th October 1937. Given his productivity at that time, another two or three of his papers would normally have been expected by March 1938.

Indeed N. Sokolov^[96] reported on a manuscript, which was in his hands at the time of Hellmann's midnight detention. However, it was lost, not unexpected under the political circumstances of that time. Furthermore, additional results from the investigations of Mamotenko should have been published. A copy of Mamotenko's dissertation on "Calculation of Interaction and Repulsion Energies in Complicated Atomic Systems" still exists in the Karpov Institute [HC44].

5.3. Kinetics of Chemical Reactions: Elementary Steps in Reactions

Chemistry as the study of change of matter naturally requires a quantum theory of elementary reaction processes and chemical kinetics. The first steps towards this end were taken by Wigner, Landau, Eyring, Hirschfelder^[65] and others in various countries. Against this background, Hellmann and Syrkin developed a general perturbation theory of wave mechanical collision processes in adiabatic and diabatic representation of the electronic states of the reacting systems [H22]. They thereby anticipated the work of Born and Huang^[7] thirty years earlier. And they were able to explain some of the extremely small factors in the Arrhenius formula for the temperature dependence of the reaction rate constants.

In his textbook Hellmann dedicated a whole chapter to the theory of nuclear dynamics, whereas two years earlier Pauling and Wilson in their book had just touched on this topic.^[66] The general formulation of coupled systems via the Schrödinger equations for nuclear dynamics in the non-adiabatic case is normally given with reference to the book by Born and Huang of 1966,^[67] but can already be found in Hellmann's book. There the main features of the semi-classical method of describing atomic and molecular collision processes are developed, adiabatic versus non-adiabatic representations are introduced, and so on.

5.4 The Textbook, a Ground-Breaking Scientific and Didactic Achievement

The history of the book

As far as can be ascertained today,^[44,68] Hellmann intended to write a review about his field of work at least from 1933 onwards. In the introduction to the German edition of the book it is stated that some "formulations in the first chapters were worked on at the time (1933) together with Prof. Dr. W. Jost (Hannover)" (see sect. 2.8, and [H16, HC16]).

The manuscript of the work, which was more or less ready in the spring of 1934, remained with Jost on Hellmann's emigration, and the former tried to find a publisher – for obvious political reasons a wasted effort. From the publishers' point of view, a welcome additional reason for refusal was that mathematical-theoretical subjects were of little interest to most German chemists. Then, by October 1935 the manuscript had been translated into Russian by three young scientists with whom Hellmann was acquainted: the nuclear physicist I.N. Golovin, the molecular physicist M.A. Kovner, and the physical chemist N.N. Tunitskij. In 1935/1936 Hellmann gave a series of lectures at the Karpov Institute, which, as also the quantum-chemical seminars, were attended by young scientists from other Moscow institutes. There probably existed close scientific contacts in the first years of Hellmann's time in Moscow between the related research groups in the area, without severe competition and jealousy concerning scientific progress, able co-workers, politically correct behavior, interpretation and selling of research results. Demarcations and hostilities between the more progressive and more politically correct university and teaching institutes, and the more rationally oriented research institutes began to flourish only in the climate of fear from the time of the Great Terror onwards.^[42]

It is easy to imagine that the young, idealistic, motivated researchers in Moscow represented a highly critical test audience for whose corrections and comments Hellmann expressed his gratitude in the preface to the Russian edition, with particular mention of his colleague and friend J. Rumer. "Quantum Chemistry" ("Kvantovaja Khimija")[H33] appeared at the beginning of 1937 in the series "Physics in Monographs", it was much sought after and was soon sold out.

While the Russian edition was still being printed, Hellmann worked on an abridged and updated German version, in order to try once again for publication in Germany. The manuscript was completed in November 1936, but negotiations with German publishers again proved difficult. Finally the publishing house of Franz Deuticke (Vienna, and also Leipzig at that time) was found, who still managed publication in 1937 [H34]. Copies left over were sold off cheaply after the war.

If the two versions are compared, it becomes clear that Hellmann tried to revise the first Russian version in order to present it in a slightly more forceful and logically compelling manner. The Russian text is rather bulky (546 pages), contains more diagrams and footnotes and makes an effort to address a largely unprepared reader. The second, German version, is more demanding, covers essentially the same material in spite of its smaller number of pages (350); it is more straightforward, but deals with a larger number of applications, and the bibliography is broader and updated. According to the preface, the German edition aims to serve as a textbook which reaches the "limits of present-day research".

The historical circumstances in which "Quantum Chemistry" originated and was publicized, as well as the tragic fate suffered by the author shortly after the appearance of the work, had the consequence that his name almost totally disappeared from scientific and public realms for about fifteen years. After World War II Hellmann was known only to few scientists, for instance Wilhelm Lenz and his group at Hamburg (e.g. Ph. D. student Heinz Werner Preuss) or Oskar Polansky at Vienna, and of course to his former colleagues at Hannover and Moscow. Neither his book nor his work played any special role at important quantum chemistry summer schools of the time, while Herrmann Hartmann in Frankfurt^[69] emphatically drew attention to him. Nevertheless, Hellmann's achievements such as his explanation of covalent bonding or his development of the pseudopotential method were sometimes acknowledged by the newly emerging generation of German quantum chemists. Hellmann's friend Syrkin in the Soviet Union had enough problems of his own and made (hardly any) mention of Hellmann in his own book.^[47]

Hellmann's book is little circulated in German^[91] and Russian speaking areas. A copy was pirated in the USA, appeared in 1944 [H34] and can be found in some American libraries. Among those who learned from his book is Roald Hoffmann.^[99]

Only rarely are Hellmann and his book taken account of in the history of science (as a counter-example, for instance,^[70] if one disregards simple remarks. It is therefore not surprising that astonishing discoveries can still be made today in this work written over 60 years ago.

Contents and Intentions pointing the Way

Hellmann's "Quantum Chemistry" was and is mostly cited in reference to the "Hellmann-Feynman Theorem", previously also known as "Feynman's Theorem" or similarly (thus from time to time in Chemical Abstracts or in ref. ^[71]; see also section 2.6). Hellmann had derived the theorem as early as 1933 [H14] for the purpose of his arguments concerning chemical bonding. The book mentions it more casually when dealing with adiabatic nuclear dynamics. ^[72] Although it seemed almost trivial in that context, it proved useful and served as the prototype of a whole family of relations of this type (cf. e.g. ^[73]).

Additionally, the book is a real treasure trove of many further research topics in quantum chemistry, which in large part have remained unknown and in several cases have been rediscovered. One example of this is the role of kinetic energy in chemical bond formation (see sections 2.7/8); another the pseudopotentials (see section 5.1). The whole work demonstrates profound understanding of physical principles, a broad overview of the current state of research, and notably, Hellmann's intimate knowledge of the area of application, i.e. chemistry. Evidence that he kept chemistry to the fore (and not atomic, molecular or solid state physics) can certainly be found in the choice of designation "quantum chemistry" for the area of knowledge he embraced.

In some respects the book bears inspection even today: its instructional procedure, its scientific content and the clarity and precision of its assertions. There is, of course, a great deal which today would be presented differently and expressed in a less antiquated way. There are parts which can be criticized. All in all, however, we have in Hellmann's "Quantum Chemistry" a significant and admirable offering by someone who by today's standards would be regarded as a really young scientist. Here he had tried to portray a wide scientific area, of only 7 years standing at the time, advanced also through his own efforts and contributions, in a work of such quality that we can still benefit from reading it more than half a century later.

6. Hellmann and the Spirit of the 1930s

6.1 Popularization of Quantum Chemistry

When scientific chemistry had started flourishing at the end of the 18th century, its leading exponents felt that they owed popularization of their discipline to the society which had supported their aims, both for the benefit of the society and of the discipline. Two examples of that time may be mentioned: Michael Faraday's "Lectures on the History of a Candle" ^[74] to young people, or Justus von Liebig's "Chemical Letters" in the *Augsburger Allgemeine Zeitung* ^[75] for a general readership.

When, after the dreadful confusion of the revolution in the Soviet Union, the natural sciences had begun to flourish ^[41,42,76] there was great willingness on the part of chemists and physicists to lecture to and write for the interested public. And the Soviet public did show great interest. Unfortunately, nowadays, there are problems with willingness to popularize science on the one hand, and with any interest being shown in it on the other. ^[77]

Already in Germany [H16, HC16], and later several times in Moscow [H18, H24, H29, H35] Hellmann had turned to the 'normal' physical chemists in order to tell them, in articles (then usually in Russian), about chemical bonding, structural aspects of inorganic and organic molecules as well as chemical reactions, using simple terms which made no great demands on their previous mathematical and physical education. He took pains to improve his instructional technique, which, of course, included some repetition. Finally Hellmann wrote a longer popular science article on the structure of matter, quantum mechanics and chemical bonding, together with some reflections on the philosophy of science. This article had originally been written in German and was published in the summer of 1936 in two issues of the Russian scientific public journal "Forefront of Science and Technology" [H30].

6.2 Interpretation of the Uncertainty Principle

Controversial debates starting in the late 1920s about the physical interpretation of the mathematical formalism of quantum mechanics ^[78] also took place in the Soviet Union. ^[42,79,80] In the above-mentioned article, Hellmann stated Lenin's opinion ^[81] that human understanding of nature was "inexhaustible" and thereby he occupied a position contrary to the so-called western "agnostic interpretation of the Uncertainty Principle". Hellmann himself [H30] said:

"At first glance it might appear that through the Heisenberg relation, human understanding of nature is, in principle, limited. In fact this is not the case, the so-called 'Uncertainty Principle' ... does not set a limit on human understanding, but on a preconception regarding the properties of matter. This preconception results from thousands of years of macroscopic experience and has attained its final and clearest form in

classical mechanics. The 'Uncertainty Principle', however, shows us with what precision the 'point mass' of classical mechanics can reproduce the behavior of the centre of gravity of real masses".

Hellmann then speaks of the "disproportion of an agnostic interpretation of the Heisenberg relation, which results from reality diverging from the preconceived anthropomorphic ideas as a shortfall of physical reality, i.e. as an imperfection in the newly developed physical laws, rather than as a lack of our unrefined powers of imagination acquired from the starkness of daily life."

Undoubtedly, for Hellmann, science took priority over ideology and politics. In any case, he took part in the debate on the Copenhagen interpretation of quantum mechanics. Thus Hellmann recognized some explanations of dialectical materialism as noteworthy accomplishments on the ideological-philosophical plane. He, himself, however, never made the slightest effort in any of his articles to ascribe the advance of science to dialectical materialism. Nevertheless, it remains to be clarified whether Hellmann's approaches to dialectical materialism were totally in agreement with his scientific convictions, and whether certain formulations were to be regarded as a tribute^[42] to the ruling ideology.

6.3 Reductionist Research Programme with Perspicuity

Hellmann advocated a reductionist, but not too formal research programme, according to which chemical phenomena should have been ascribed to basic physical laws. He attempted a "direct graphic ("anschaulich") understanding of the basic properties of matter referred to by the Schrödinger equation, and from this to derive the laws of the chemical structure of matter" [H30]. In his publications he always stressed the graphic nature of the new wave mechanics as a whole, and specifically the possibility of a clear understanding of how the homeopolar valency arises.

What did Hellmann mean by "directly graphic" ("unmittelbar anschaulich") or "graphic understanding of the theory"? He gives us to understand that diagrammatical imagination of physical objects and models, linked with mathematical formalism, is to be seen as a metaphor. Hellmann based his work on three distinct metaphors regarding electrons. Firstly, the classical particle picture of a "moving point charge" in three-dimensional real space. Secondly, the statistical picture after Fermi, where the electrons form an "atmosphere" around the nucleus, which is described in six-dimensional phase-space. And thirdly, the wave-picture based on the Schrödinger equation. In his "Quantum Chemistry" [H34] he noted: "...the statistical picture by virtue of its close analogy to classical thermodynamics is particularly useful in quantum chemistry."

Hellmann may even then have encountered difficulties with the 'proper chemists' because abstract phase space ideas of thermodynamics became the centre of explanations. This is probably what Erich Hückel alluded to in a letter to H. Hartmann at the beginning of 1940, when he wrote that "Hellmann's book is fairly dogmatic, after all [...], and the link with a chemist's way of thinking is missing. Nevertheless, one can, of course, learn a great deal from it".^[82] The "missing link to a chemist's way of thinking" was a characteristic, however, of the German founders of quantum chemistry (as, for instance, Hund, see section 2.4) since those were purely theoretical physicists. They were not very interested in specific chemical problems, and were content to have - more or less - solved the problem of chemical bonding "in principle". In contrast to this, the first two articles by Hellmann and Jost on "Understanding Chemical Forces according to Quantum Mechanics" in the periodical "Zeitschrift für Elektrochemie und angewandte Physikalische Chemie" [H16, HC16] were especially noted and accepted by Otto Schmidt, particularly because of their "clear and easily usable representation of homeopolar valency",^[83] when he did basic work on the theory of pair bonding in the "Principal Laboratory" of I.G. Farben at Ludwigshafen. The above criticism by E. Hückel therefore applies to Hellmann only in a very limited way.

7. Epilogue: "Life" under Stalin – Arrest, Murder, Rehabilitation

"He invents a formula and afterwards jumps around it with a slide rule", these are the words used by Michail Tjomkin (=Temkin), the group leader of technical heterogenous catalysis at the Karpov Institute, to describe his quantum chemistry colleague Hellmann. That was after the German scientist had disappeared from the Institute in March 1938.^[84] It is now uncertain whether this is simply a friendly anecdote about Hellmann's enthusiasm for his formal science, or whether it contains scientific reservations of an empirical versus a theoretical scientist, or even the spite of an informer. Some colleagues at the institute recognized that Tjomkin did not like Hellmann's work.^[84] Hellmann felt that not all chemists understood his work on the borderline of physics, and that perhaps he was no longer in the right place at the Karpov Institute. Similarly, though perhaps in Russia less than in Germany, 'regular experimental chemists' had reservations about the new quantum theory; especially if basic mathematical

knowledge was missing, to grasp the outline of the theory. On the other hand, there were many open-minded colleagues, quite apart from the scientists working in similar fields at the Karpov Institute and other research and university facilities.^[96]

Towards New Year 1938 however, Hellmann mentioned in a letter that he had trouble at the Institute. He would have liked to change to the Academy of Sciences (a refuge for scientists of politically incorrect theoretical physics)^[42] but for this his knowledge of Russian was insufficient.^[44]

When Viktoria, Hellmann's wife, went to the Institute a few days after his arrest to collect his salary – which she was not given – she saw a denunciation against her husband in a news bulletin on the wall, signed by Zhukhovitskij and Tjomkin.^[84,85] Whether lack of scientific esteem or envy of a colleague caused this step against the young and very successful foreigner cannot be determined in retrospect. Anyhow, Tjomkin was a scientifically as well as personally highly esteemed and respected colleague among the scientists working at the Karpov Institute. He had been the Party Secretary of the Institute for some time. However, this post was now held by Zhukhovitskij.^[97] He was Hellmann's close colleague [H24], he was considered clever, but unlike Hellmann, had not written anything fundamental regarding quantum chemistry, according to the theoretical chemist Tatjevskij.^[86] By the way, Tatjevskij later 'criticized' Syrkin publicly and blamed him for accepting the principle of VB-superposition and Pauling's resonance concept. No positive comments on the human qualifications of Zhukhovitskij could now be obtained at the Karpov Institute. Many of the scientists of the time were said to exclude scientific competitors by denunciation in order to further their own careers.^[41(p.108), 89] Zhukhovitskij, at least, reaped direct benefit from Hellmann's arrest, since he took over the latter's research group and students. Zhukovitskij had probably received orders from the secret service^[42] to open dossiers on all possible saboteurs in his area of service, and in 1937 this included, for instance, all Germans living in the Soviet Union. So far it is unknown whether Zhukhovitskij had received party orders to create and sign the wall bulletin mentioned.

Vjacheslav Molotov, who fought with Stalin and was one of those mainly responsible for the Terror, said in a conversation in the 1960s, that in 1937 "there still remained enemies of all colours, who might unite in the danger of fascist aggression. We have to thank the year 1937 that we had no fifth column during the war [due to the] prophylactic cleansing without fixed limits. The most important thing was not to overlook any enemies, the number of innocent victims was a secondary issue."^[87(p.258)]

In addition to Stalin's and his Politburo's paranoid fear of political enemies it was said to become necessary, by the end of the 1930s, to guard against spies and saboteurs from abroad. The pre-war period had begun early, also in the Soviet Union. The 'addresses' for the mass repressions against the alleged 'fifth column' – an expression from the Spanish civil war – had been decided upon by the February/March 1937 Plenum of the Politburo. Amongst the targets were the "suspicious nationalities", i.e. Germans, Poles, Koreans, Jews and others.^[87(p.260)] Those in high political circles had set quotas for each region concerning the number of foreigners to be arrested and prosecuted.^[42,76]

The public was able to discern the new trends from the media. In an official propaganda campaign German fascism was combined with Trotskyism, i.e. the exterior with the interior enemy: "Spies, contemptible hirelings of fascism, traitors of the homeland – shoot them dead!"^[89(p.22ff)] Many Russians were now frightened of having contact with Germans,^[89(p.17ff)] since every arrest led to further arrests, not just because the accused accused others, but because according to cleansing logic those who knew a culprit were guilty themselves.^[42]

If Hans Hellmann had been doomed in Germany because his wife was Jewish, he was now doomed to suffer from his own nationality. The only personal evidence we have from him are his letters, where, of course, he had to consider censorship. In 1937 Hellmann wrote to the German relatives in terms now sounding strangely distant, that "foreigners were no good, they would vanish".^[44(Christmas 1937)] Perhaps this was meant to express that he, too, was afraid for his life. Except for one remark about trouble at the Institute, about which he gave no further details, he did not mention any possible friction, nor did he say with whom he was involved in disputes.^[44(autumn 1937)] Only at the New Year 1937/8 did he express himself more clearly: "Dear mother, it is certainly not neglect on my part that I don't write more often. You do have some idea of the present international situation. The mood seems almost pre-war, so I am really afraid to engage in too much correspondence with other countries. In fact, the wall between us gets higher every day".^[44] The German school at Trubnaja Square, which the son Hans jr. had been attending, was closed, and books sent from Germany no longer arrived.

In the night from 9th to 10th March 1938, Hans Hellmann was arrested by men in dark coats and taken to Taganka prison. The whole apartment was rifled.

The documents remaining about Hellmann in the NKWD archives contain no record of a hearing but of an interrogation.^[42(p.192ff)] It contains a short hand-written confession dated 13th March, which was not written by Hellmann himself, but signed by him in a faint hand. The contents accused him of espionage: he was said to have been recruited for the secret service by the assistant Gussmann, a Nazi at the TiHo in Hannover and to have passed – via a Polish colleague^[93] – documents about the Karpov Institute, production of poison gas etc. to Germany. The record states that there was no proofs of this.

Hellmann's personal staff record shows the order for him to be shot, authorized by the Public Prosecutor of the USSR, Andrej Vyshinskij.^[90] Hellmann was given the maximum sentence on 17th May and shot on 29th May 1938. He had thus become one of the many hundred thousands of innocent victims of Soviet mass repressions of 1937-8.

As early as 1937 the mass arrests had been noticed abroad. On 16th May Albert Einstein submitted a petition to Stalin in which he expressed the hope that "great care be taken in proceedings concerning people of rare energy and ability". A letter with similar content was sent on 18th June to the Public Prosecutor by the three Nobel laureates Irène Joliot-Curie, Frédéric Joliot-Curie and Jean-Baptiste Perrin. Their pleas were not heard, the cleansing machine continued mercilessly on its way.

Hellmann's fate remained unknown until 1957. On the 15th October 1957 his wife and son were granted complete rehabilitation.^[93] This became known in the 1960s to some scientists in the West.^[97] But it was not until August 1989 that the Hellmanns came to know the truth about his death.

Hellmann's tragedy continued in his family. His wife Viktoria and his son were evicted from the staff apartment. At first Viktoria was able to work outside Moscow as a teacher of German. In 1941, she, too, was denounced and spent eight months in the Moscow Butyrkij prison, before she was banned to a camp in Kasakhstan. The son was 11 years old when she was arrested, and he was to be taken to a special children's home, but he managed to escape and hide with relatives. He did not meet his mother again until 1956, the year of the famous 20th Party Congress and Khrushchjov's destalinization. The son survived under the new identity of Genadij Minchin and was not able to recover his original name before 1989.

Hellmann was still searched by Nazi Germany for years after his death. This is evident from an inquiry by the review commission for safeguarding German literature dated May 1944, and the entry of his name into the "Special USSR wanted list"^[92] the book used for "searches" by the German operational groups in the Russian campaign of 1941.

The tragic fate of the Hellmann family, documented here in appreciation of Hans Hellmann's scientific achievements, reminds us to keep in mind those, who became victims of the oppressors in ideological warfare.

Appendix: Hellmann's Publications

All of Hellmann's works (with "H" in front of the running number), as far as they have become known to us, are listed here. They are arranged (mainly) chronologically according to the date of receipt of the manuscripts (given in parentheses).

References with "HC" followed by a number refer to work by Hellmann in co-operation with colleagues and co-workers, where the fact that Hellmann was a co-author was not or could no longer be mentioned in the German Reich or in the Soviet Union for political reasons.

Names printed in cyrillics were transliterated according to the rules given in the Register of Authors of Chemical Abstracts, with slight variations: "i-kratkoje" = j, ë = jo. The languages of the articles are indicated by letters (G = German, E = English, R = Russian).

A lower case g indicates the availability of a German translation in the Hellmann-Archive. Original issues of reprints and books available in the Hellmann-Archive are indicated by a fat letter **O**, otherwise copies exist.

A1 Kiel und Stuttgart (1925-1929)

- [H1] **H. Hellmann, H. Zahn** (Kiel - 14.09.1925). *A new method of determining the dielectric constant of highly conductive electrolyte solutions.* Phys. Z. 26 (**1925**) 680-682.
G
- [H2] **H. Hellmann, H. Zahn** (Kiel - 11.04.1926). *The dielectric constants of well conducting electrolyte solutions.* Ann. Phys. (Leipzig) [4] 80 (**1926**) 191-214.
G
- [H3] **H. Hellmann, H. Zahn** (Kiel / Stuttgart - 12.08.1926). *On the dielectric constant of diluted aqueous electrolyte solutions.* Phys. Z. 27 (**1926**) 636-640.
G
- [H4] **H. Hellmann, H. Zahn** (Kiel / Stuttgart - 28.08.1926). *The dielectric constants of well conducting electrolyte solutions. (part 2).* Ann. Phys. (Leipzig) [4] 81 (**1926**) 711-756.
G
- [H5] **H. Hellmann, H. Zahn** (Kiel / Stuttgart - 14.12.1927). *On dielectric constants of electrolyte solutions. Response to an article of same title by P. Walden, H. Ulich and O. Werner.* Z. Phys. Chem. Stöchiom. Verwandtschaftsl. 132 (**1928**) 399-400.
G
- [H6] **H. Hellmann, H. Zahn** (Kiel / Stuttgart - 21.05.1928). *On dielectric constants of electrolyte solutions. Response to an article of same title by P. Walden, H. Ulich and O. Werner.* Ann. Phys. (Leipzig) [4] 86 (**1928**) 687-716.
G
- [H7] **H. Hellmann, H. Zahn** (Kiel - 01.10.1928). *Supplement to our work: On dielectric constants of electrolyte solutions.* Ann. Phys. (Leipzig) [4] 87 (**1928**) 716.
G
- [H8] **H. Hellmann** (Stuttgart - 03.04.1929). *Analysis of absorption curves for incidence from all directions of inhomogeneous radiation at planar interfaces..* Phys. Z. 30 (**1929**) 357-360.
G
- [H9] **H. Hellmann** (Stuttgart - 07.07.1929). *On the appearance of ions upon decay of ozone and the ionization of the stratosphere.* Ann. Phys. (Leipzig) [5] 2 (**1929**) 707-732. - This is the published version of Hellmann's Ph.D. (Dr.-Ing.) dissertation, carried through at the Physical Institute of the Stuttgart Institute of Technology, delivered on April 6, 1929 (the longer original version is no longer available in the university library). Referees were Prof. Dr. **Erich Regener** and Prof. Dr. Richard Glockner. Regener let his students publish their Ph.D. works under their sole authorships.
G,**O**

A2 Hannover (1930-1934)

- [H10] **E. Fues, H. Hellmann** (Hannover, TH - 22.03.1930). *On polarized electron waves.* Phys. Z. 31 (**1930**) 465-478.
G
- [H11] **H. Hellmann** (Hannover, TH - 24.03.1931). *On crystal interferences of the spin-electron.* Z. Phys. 69 (**1931**) 495-506.
G,**O**
- [H12] **H. Hellmann** (Hannover, TH - 22.06.1931). *Supplement to my paper: "On crystal interferences of the spin-electron".* Z. Phys. 70 (**1931**) 695-698.
G
- [H13] **H. Hellmann** (Hannover, TiHo - 01.03.1933). *On the quantum mechanics of the chemical valence.* Z. Phys. 82 (**1933**) 192-223.
G,**O**

- [H13a] **H. Hellmann** (Hannover, TiHo – 05.02.1933). *On the quantum theory of atomic binding*
G [conference abstract]. Verh. Deutsch. Phys. Ges. [3] 14 (1) (1933) 13-14
- [H14] **H. Hellmann** (Hannover, TiHo – 20.07.1933). *On the role of the kinetic electronic energy for the*
G,O *interatomic forces*. Z. Phys. 85 (1933) 180-190.
- [H14a] **H. Hellmann** (Hannover, TiHo – 15.07.1933). *On the role of the kinetic electronic energy for the*
G *interaction between atoms* [title of conference talk]. Verh. Deutsch. Phys. Ges. [3] 14 (2) (1933)
27
- [H15] **H. Hellmann** (Hannover, TiHo – 24.01.1934). *An absolute method of measurement of dielectric*
G,O *constants of electrolyte solutions at high frequency*. Ann. Phys. (Leipzig) [5] 19 (1934) 623-636.
- [HC15] **M. Röver** (Hannover, TiHo – 07.08.1934). *Measurement of dielectric constants of aqueous*
G *electrolyte solutions at high frequency*. Ann. Phys. (Leipzig) [5] 21 (1934) 320-344.
- [H16] **H. Hellmann, W. Jost** (Hannover, TiHo und TH – 13.10.1934). *Understanding the "chemical*
G *forces" according to quantum mechanics*. Z. Elektrochem. Angew. Phys. Chem. 40 (1934) 806-
814.
- [HC16] **W. Jost** (Hannover, TH – 01.08.1935). *Understanding the "chemical forces" according to*
G *quantum mechanics. Part II*. Z. Elektrochem. Angew. Phys. Chem. 41 (1935) 667-674. („As in
part I, the presentation is extensively based on the reasoning of Hellmann's papers.“)

A3 Moscow (1934-1937)

- [H17] **G. Gel'man / H. Hellmann** (Moscow – 10.06.1934). *On a combined perturbation procedure in*
R,G *the problem of many electrons*. C. R. Acad. Sci. URSS N.S. (Dokl. Akad. Nauk SSSR) 4 (1934)
442-444 (in Russian), 444-446 (in German).
- [H18] **H. Hellmann** (Moscow – 11.07.1934) *On the nature of the chemical forces* (in German). Acta
G,O Physicochim. U.R.S.S. 1 (1934/1935) 333-353.
- [H19] **H. Hellmann** (Moscow – 26.11.1934). *A New Approximation Method in the Problem of Many*
E *Electrons*. J. Chem. Phys. 3 (1935) 61.
- [H20] **H. Hellmann** (Moscow – 17.12.1934). *A combined approximation procedure for calculation of*
G,O *energies in the problem of many electrons* (in German). Acta Physicochim. U.R.S.S. 1
(1934/1935) 913-940.
- [H21] **H. Hellmann** (Moscow – 05.04.1935). *On the quantum mechanical calculation of polarizabilities*
G,O *and dispersion forces* (in German). Acta Physicochim. U.R.S.S. 2 (1935) 273-290.
- [H22] **H. Hellmann, J. K. Syrkin** (Moscow – 05.05.1935). *On the question of anomalously small steric*
G,O *factors in chemical kinetics* (in German). Acta Physicochim. U.R.S.S. 2 (1935) 433-466.
- [H23] **H. Hellmann** (Moscow – 01.07.1935). *Remarks on the polarization of electron waves by*
G,O *scattering* (in German). Z. Phys. 96 (1935) 247-250.
- [H24] **G. G. Gel'man, A. A. Zhukhovitskij**. ([without place] – [without date]). *The fundamental*
R,g *questions of chemical reactions in present-day quantum chemistry* (in Russian). Usp. Khim. 4
(1935) 1149-1193.
- [H25] **H. Hellmann** (Moscow – 03.12.1935). *A combined approximation procedure for the calculation*
G *of energies in the problem of many electrons* (in German). II. Acta Physicochim. U.R.S.S. 4
(1936) 225-244.
- [H26] **H. Hellmann** (Moscow – 03.02.1936). *Comments on the work of E. L. Hill „The virial theorem*
G *and the theory of fusion“* (in German). Phys. Z. Sowjetunion 9 (1936) 522-528.
- [H27] **H. Hellmann, W. Kassatotschkin** (Moscow – 15.03.1936). *Metallic Binding According to the*
E *Combined Approximation Procedure*. J. Chem. Phys. 4 (1936) 324-325.
- [H28] **H. Hellmann, W. Kassatotschkin** (Moscow – 16.05.1936). *Metallic Binding According to the*
G *Combined Approximation Procedure* (in German). Acta Physicochim. U.R.S.S. 5 (1936) 23-44.

- [H29] **G. G. Gel'man** ([without place] – 22.07.1936). *The application of the Thomas-Fermi method on the problem of chemical binding* (in Russian). Usp. Khim. 5 (1936) 1373-1404.
R,g
- [H30] **G. Gel'man**. ([without place] – [without date]). *The Nature of Matter in the light of quantum chemistry* (in Russian). Front Nauki Tekh. (1936) 6: 34-48, 7: 39-50. – Original manuscript in German, 47 pages.
R,g,O
- [H31] **H. Hellmann** (Moscow – [09./10. 1936]). [*Contributed Discussions to: F. London. The general theory of molecular forces*]. Trans. Faraday Soc. 33 (1937) 40-42, 278-279.
E
- [H32] **H. Hellmann** (Moscow – [09./10. 1936]). [*Contributed Discussion to: Samuel Glasstone. The structure of some molecular complexes in the liquid phase*]. Trans. Faraday Soc. 33 (1937) 208-209.
E
- [H33] **G. Gel'man** (Moscow - 23.10.1936). "*Quantum Chemistry*" (German manuscript translated into Russian by J. Golovin, N. Tunitskij, M. Kovner). ONTI, Moscow and Leningrad (1937). 546 p.
R,O
- [H34] **H. Hellmann** (Moscow – 03.1937). "*Einführung in die Quantenchemie*" (Introduction to quantum chemistry, in German). Deuticke, Leipzig and Wien (1937), VIII + 350 p.
G,O
- [H35] **G. Gel'man** ([without place] - 23.01.1937). *The problem of valency in present-day organic chemistry* (in Russian). Prom-st. Org. Khim. 3 (1937) 259-266
R,g
- [H36] **H. Hellmann, K. Majewski** (Moscow – 11.04.1937). *On the calculation of London's Dispersion forces at small inter atomic distances* (in German). Acta Physicochim. U.R.S.S. 6 (1937) 939-953.
G
- [H37] **H. Hellmann, M. Mamotenko** (Moscow – 29.04.1937). *The determination of electron affinities and valence states with the help of new interpolation formulas in the theory of complex spectra* (in German). Acta Physicochim. U.R.S.S. 7 (1937) 127-147.
G
- [H38] **H. Hellmann, S. J. Pschejtzkij** (Moscow – 26.06.1937). *On the quantum theory of polarizabilities of atoms and ions in inhomogeneous electric fields* (in German). Acta Physicochim. U.R.S.S. 7 (1937) 621-645.
G
- [H39] **M. Mamotenko, G. Gel'man** (Moscow – 07.10.1937). *Calculation of the electron affinities of metallic atoms* (in Russian). Zh. Eksp. Teor. Fiz. 8 (1938) 24-30
R,g
- [H40] **M. Mamotenko, H. Hellmann** (Moscow – 11.10.1937). *The calculation of electron affinities with the help of new extrapolation formulas for optical terms. II* (in German). Acta Physicochim. U.R.S.S. 8 (1938) 1-8.
G

A4 Moscow (after 1937)

- [HC41] **N. Sokolov** (Moscow – 1938). *Application of the Thomas-Fermi method including Weizsäcker's extension of the statistical model of atoms* (in Russian). Zh. Eksp. Teor. Fiz. 8 (1938) 365-376
R
- [HC42] **S. J. Pschejtzkij** (Moscow – 1938). *The polarization of ions in inhomogeneous fields and the calculation of the dissociation energy of ionic molecules* (in German). Acta Physicochim. U.R.S.S. 11 (1938) 793-800
G
- [HC43] **M. A. Kovner** (Moscow – 20.03.1942). *Quantum theory of the ammonia molecule*. C.R. Acad. Sci. URSS N.S. (Dokl. Akad. Nauk SSSR) 35 (1942) 177-179 (in English), 197-199 (in Russian).
R,g
- [HC44] **M. Mamotenko** (Moscow – 1941). *Calculation of interaction and repulsion energies in complicated atomic systems* (in Russian). Dissertation, Karpov Institute of Physical Chemistry.
R,(g)
- [HC44a] **G. Gel'man, M. Mamotenko** (Moscow – 1938). A manuscript which no longer exists had been in the hands of N. Sokolov.
R
- [H34'] **H. Hellmann** (Moscow – 03.1937). "*Einführung in die Quantenchemie*" (Introduction to quantum chemistry, in German). Reprint (War alien reproduction), J. W. Edwards, Ann Arbor, Michigan (1944), VIII + 350 p.
G

References

- [1] P. Debye, E. Hückel, Phys. Z. 24 (1923) 185, 305; E. Hückel, Phys. Z. 26 (1925) 116; P. Debye, *Polare Molekeln*, Hirzel, Leipzig (1929); L. Onsager, Phys. Z. 27 (1926) 388; 28 (1927) 277; P. Debye, H. Falkenhagen, Phys. Z. 29 (1928) 121, 401; H. Falkenhagen, *Elektrolyte*, Hirzel, Leipzig (1932)
- [2] P. Walden, H. Ulich, O. Werner, Z. Phys. Chem. 115 (1925) 178, 129 (1927) 417
- [3] J.G. Kortüm, *Elektrolytlösungen*, Akademische Verlagsgesellschaft, Leipzig (1941); H. Falkenhagen, *Elektrolyte*, 2. Ed., Hirzel, Leipzig (1953)
- [3a] J.G. Barthel, H. Krienke, W. Kunz, *Physical Chemistry of Electrolyte Solutions. Modern Aspects*, Steinkopff, Darmstadt (1998)
- [4] U. Dehlinger, in *Reden und Aufsätze*, TH Stuttgart, 21 (1956) 39; W. Bothe, Z. Naturforsch. A 6 (1951) 565
- [5] K. Gavroglu, *Fritz London, a scientific biography*, Cambridge University Press, Cambridge (1995); A. I. Simoes, *Converging trajectories, diverging traditions: chemical bond, valence, quantum mechanics and chemistry 1927-1937*, Dissertation, University of Maryland (1993)
- [6] K. Gavroglu, A. Simoes, *The Americans, the Germans and the beginnings of quantum chemistry*, Hist. Stud. Phys. Biol. Sci. 25/1 (1994) 47-110
- [7] W. Heitler, F. London, Z. Phys. 44 (1927) 455.
- [8] J.H. van Vleck, Chem. Rev. 5 (1928) 467
- [9] L. Pauling, Chem. Rev. 5 (1928) 173
- [10] J.C. Slater, *Introduction to Chemical Physics*, McGraw-Hill, New York (1939)
- [11] A. Haas, *Die Grundlagen der Quantenchemie. Eine Einleitung in vier Vorträgen*, Akademische Verlagsgesellschaft, Leipzig (1929)
- [12] A. Sommerfeld et al., Contributions to the Main Conference Topic: "*Die Arten der chemischen Bindung und der Bau der Atome*", Z. Elektrochem. Angew. Phys. Chem. 34 (1928) 426-546
- [13] H. Falkenhagen, Ed., *Quantentheorie und Chemie*, Leipziger Vorträge 1928, Hirzel, Leipzig (1928)
- [14] W.E. Garner, J.E. Lennard-Jones et al., Contributions to the meeting on "*Molecular Spectra and Molecular Structure*", Trans. Faraday Soc. 25 (1929) 611-949
- [15] G.L. Clark, Chem. Rev. 5 (1928) 361, and following articles
- [16] N.F. Mott, Proc. Roy. Soc. London A 124 (1929) 425; N.F. Mott, H.S.W. Massey, *The Theory of Atomic Collisions*, third ed., section IX, Clarendon, Oxford (1965)
- [17] V. Weisskopf, Z. Phys. 93 (1935) 561
- [18] G. P. Thomson, Philos. Mag. 17 (1934) 1058; Th. Förster, Z. Phys. 85 (1933) 514
- [19] E.S. Dymond, Proc. Roy. Soc. London A 145 (1934) 657; R.A. Smith, Proc. Cambridge Philos. Soc. 30 (1934) 520
- [20] A.E. van Arkel, J.H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, German edition from L. and W. Klemm, Hirzel, Leipzig (1931), with cooperation of Biltz and Fischer. §11, p. 40-48, and §52, p. 288-300, edited by H. Hellmann
- [21] W. Kossel, Ann. Phys. (Leipzig) [4] 49 (1916) 229; *Valenzkräfte und Röntgenspektren*, 2. Ed., Springer, Berlin (1924)
- [22] M. Born, Verh. Deutsch. Phys. Ges.[2] 21 (1919) 13, 679; F. Haber, *ibid.* 750; K. Fajans, *ibid.* 539, 714
- [23] F. London, in [12], p. 59; F. Hund, *Ergeb. exakten Naturwiss.* 8 (1929) 147; in *Handbuch der Physik*, 2. Ed., Eds. H. Geiger, K. Scheel, Vol. 24/2, Springer, Berlin (1933) 368; W. Heitler, Phys. Z. 31 (1930) 185, in *Handbuch der Radiologie* 4/2, p. 485, Akademische Verlagsgesellschaft, Leipzig (1934); M. Born, *Ergeb. exakten Naturwiss.* 10 (1931) 387; G. Herzberg, in *Molekülstruktur*, Leipzi-

- ger Vorträge 1931, Ed. P. Debye, Hirzel, Leipzig (1931), p. 167; N.V. Sidgwick, *Some Physical Properties of the Covalent Link in Chemistry*, Cornell University Press, New York (1933)
- [24] W. Heitler, F. London, Z. Phys. 44 (1927) 455; F. London, Z. Phys. 46 (1928) 455, 50 (1928) 24; W. Heitler, Z. Phys. 47 (1928) 835; W. Heitler, G. Rumer, Z. Phys. 68 (1931) 12, Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl. (Göttinger Nachr.) (1930) 277; H. Weyl, *ibid* (1930) 285
- [25] J.C. Slater, Phys. Rev. 37 (1931) 481
- [26] L. Pauling, J. Am. Chem. Soc. 53 (1931) 1367; J. Chem. Phys. 1 (1933) 280; L. Pauling, G.W. Wheland, J. Chem. Phys. 1 (1933) 362
- [27] F. Hund, Z. Phys. 51 (1928) 759
- [28] J.C. Slater, Phys. Rev. 38 (1931) 1109
- [29] R.S. Mulliken, Phys. Rev. 32 (1928) 186, 761 and many further papers
- [30] E. Hückel, Z. Phys. 70 (1931) 204, 76 (1932) 628, Z. Elektrochem. Angew. Phys. Chem. 43 (1937) 752, 827
- [31] F.O. Ellison, J. Am. Chem. Soc. 85 (1963) 3540; J.C. Tully, R.K. Preston, J. Chem. Phys. 55 (1971) 652; T. Arai, Rev. Mod. Phys. 32 (1960) 370; A.C. Hurley, Rev. Mod. Phys. 35 (1963) 448; P.J. Kuntz in *Theoretical Models of Chemical Bonding*, part 2, *The Concept of the Chemical Bond*, Ed. Z.B. Maksic, Springer, Berlin (1990) p. 321
- [32] R. McWeeny, Proc. Roy. Soc. London A 223 (1953) 63
- [33] V. Fock, Phys. Z. Sowjetunion 1 (1932) 497
- [34] J. C. Slater, J. Chem. Phys. 1 (1933) 687
- [35] R.P. Feynman, Phys. Rev. 56 (1939) 340
- [36] E. Schrödinger, Ann. Phys. (Leipzig) [4] 80 (1926) 437; W. Pauli, in *Handbuch der Physik*, 2. Ed., Eds. H. Geiger, K. Scheel, Bd. 24/2, p.83, Springer, Berlin (1933)
- [37] K. Ruedenberg, Rev. Mod. Phys. 34 (1956) 326
- [38] W. Kutzelnigg, Angew. Chem. 85 (1973) 551, Angew. Chem. Int. Ed. Engl. 12 (1973) 46
- [39] R.S. Mulliken, W.C. Ermler, *Diatomic Molecules*, Academic Press, New York (1977)
- [40] M. Schimanski, *Die Tierärztliche Hochschule Hannover im Nationalsozialismus*, Dissertation, TiHo Hannover (1997).
- [41] D. Beyrau, *Intelligenz und Dissens. Die russischen Bildungsschichten in der Sowjetunion 1917-1985*. Vandenhoeck und Ruprecht, Göttingen (1993)
- [42] G. Gorelik: "Meine antisowjetische Tätigkeit..." *Russische Physiker unter Stalin*. Vieweg, Braunschweig (1995)
- [43] B. N. Finkelstein, G. E. Horowitz, Z. Phys. 48 (1928) 118, 448
- [44] Letters of Hellmann to Germany, April 1934 - January 1938, in the "Hellmann-Archive" in Siegen University (Prof. W.H.E. Schwarz)
- [45] A.P. Simonov, Zh. Fis. Khim. 10 (1993) 1957; Printed Document, *The State Scientific Centre of Russian Federation. Karpov Institute of Physical Chemistry*, Moscow (1998). Copies in the "Hellmann-Archive".
- [47] Y.K. Syrkin, M.E. Djatkina, *Chemical Bonding and Molecular Structure* (in Russian). Moscow (1946); *Structure of Molecules and the Chemical Bond*. Butterworths, London (1950) and Dover, New York (1964)
- [48] "Shockwork": Additional mobilization of work with especial results; the most famous "Shock Worker" (official honorary title since 1935) of Soviet history was the mine worker Stakhanov. Copies in the "Hellmann-Archive"
- [49] J. Sauer, Bunsenmagazin 1 (1883) 3 [46] Archive of the Karpov Institute: Type-Script 175-13. *Karpov-State-Institute of physical Chemistry* (in Russian). Moscow (ca. 1936); Personnel files

- [50] W.H.E. Schwarz, E.M. van Wezenbeek, E.J. Baerends, J.G. Snijders, *J. Phys. B* 22 (1989) 1515
- [51] W.H.E. Schwarz, *Nachr. Chem. Techn. Lab.* 35 (1987) 178
- [52] L.H. Thomas, *Proc. Cambridge Phil. Soc.* 23 (1926) 542; E. Fermi, *Z. Phys.* 36 (1926) 902, 48 (1928) 73; *Rend. Acc. Lincei* [6] 6 (1927) 602; P.A.M. Dirac, *Proc. Roy. Soc. London A* 112 (1926) 661, *Proc. Cambridge Phil. Soc.* 26 (1930) 376
- [53] G. Frenking, I. Antes, M. Böhme, S. Dapprich, A.E. Ehlers, V. Jonas, A. Neuhaus, M. Otto, R. Stegmann, A. Veldkamp, S.F. Vyboishchikov, *Rev. Comp. Chem.* 8 (1996) 63; T.R. Cundari, M.T. Benson, M.L. Lutz, S.O. Sommer, *Rev. Comp. Chem.* 8 (1996) 145; M. Dolg, H. Stoll, *Handbook Phys. Chem. Rare Earths* 22 (1996) 607
- [54] W.H.E. Schwarz, *Theoret. Chim. Acta* 11 (1968) 307, 377, 15 (1969) 235; *Acta Phys. Acad. Sci. Hung.* 27 (1969) 391
- [55] P. Gombás, *Z. Phys.* 94 (1935) 473; s.a. *Pseudopotentiale*. Springer, Wien (1967)
- [56] J.C. Phillips, L. Kleinman, *Phys. Rev.* 116 (1959) 287, 880; 17 (1960) 460; 118 (1960) 1153; I.V. Abarenkov, V. Heine, *Phil. Mag. (Ser. 8)* 12 (1965) 529
- [57] H. Preuß, *Z. Naturforsch.* 10a (1965) 365; L. Szasz, G. McGinn, *J. Chem. Phys.* 42 (1965) 2363; W. Kutzelnigg, R. Koch, W.A. Bingel, *Chem. Phys. Lett.* 2 (1968) 197
- [58] P.M.A. Dirac, *Proc. Roy. Soc. A* 123 (1929) 714
- [59] W.H.E. Schwarz, *Theoret. Chim. Acta* 23 (1971) 147; P. Hafner, W.H.E. Schwarz, *J. Phys. B.* 11 (1978) 217 (received 23.6.1977); Y.S. Lee, W.C. Ermler, K.S. Pitzner, *J. Chem. Phys.* 67 (1977) 5861 (received 25.7.1977)
- [60] F. London, *Z. Phys. Chem. B* 11 (1930) 222; J.C. Slater, J.G. Kirkwood, *Phys. Rev.* 31 (1931) 682; J.G. Kirkwood, *Phys. Z.* 33 (1932) 57
- [61] L. Pauling, Y. Beach, *Phys. Rev.* 47 (1935) 686
- [62] R.D. Shannon, *Acta Cryst. A* 32 (1976) 752
- [63] R.G. Pearson, *J. Am. Chem. Soc.* 85 (1963) 3533; I. Fleming, *Frontier Orbitals*. Wiley, Chichester (1976)
- [64] H. Hotop, W.C. Lineberger, *J. Phys. Chem. Ref. Data* 4 (1975) 539; 14 (1985)
- [65] H. Pelzer, E. Wigner, *Z. Phys. Chem. B* 15 (1932) 445; L. Landau, *Phys. Z. Sowjetunion* 2 (1932) 46; H. Eyring, *J. Chem. Phys.* 3 (1936) 107; J. Hirschfelder, H. Eyring, B. Topley, *J. Chem. Phys.* 4 (1936) 170; M.G. Evans, M. Polanyi, *Trans. Faraday Soc.* 31 (1935) 875
- [66] L. Pauling, E.B. Wilson, *Introduction to Quantum Mechanics. With Applications to Chemistry*. McGraw Hill, New York (1935)
- [67] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*. Clarendon Press, Oxford (1966)
- [68] W. Jost, *Annu. Rev. Phys. Chem.* 17 (1966) 1
- [69] H. Hartmann, *Theorie der chemischen Bindung auf quantentheoretischer Grundlage*. Springer, Berlin (1954)
- [70] A. Karachalios, *Mitt. Ges. Deutsch. Chem. Fachgr. Gesch. Chem.* 13 (1997) 163
- [71] J.C. Slater, *Quantum Theory of Molecules and Solids. Vol I. Electronic Structure of Molecules*. McGraw-Hill, New York (1963)
- [72] In chapter IX, §80 of the Russian Edition [H33], and, respectively, in chapter VIII, §54 of the revised German Edition [H34]
- [73] L. Züllicke, *Quantenchemie - Ein Lehrgang. Band 1: Grundlagen und allgemeine Methoden*. Hüthig, Heidelberg (1978)
- [74] M. Faraday, *Naturgeschichte einer Kerze*. (Chemical History of a Candle), Franz Becker, Bad Salzdetfurth (1979)
- [75] J. Liebig, *Chemische Briefe*. (Familiar Letters on Chemistry). Winter, Heidelberg (1844)

- [76] S. Courtois, N. Werth, J.-L. Panné, A. Paczkowski, K. Bartosek, J.-L. Margolin, *Das Schwarzbuch des Kommunismus. Unterdrückung, Verbrechen und Terror*. (The Block Book of Communism). Piper, München (1997, ²1998); R. Conquest, *Der Große Terror. Sowjetunion 1934-1938*. Langen-Müller, München (1992)
- [77] U. Schnabel, *Ware Wissenschaft*. Die Zeit 54-6 (4.2.1999) 27f
- [78] M. Jammer, *The Conceptual Development of Quantum Mechanics*. McGraw Hill, New York (1966); *The Philosophy of Quantum Mechanics*. Wiley, New York (1974); K. Baumann, R.U. Sexl, *Die Deutungen der Quantentheorie*. Vieweg, Braunschweig (1984); F. Selleri, *Die Debatte um die Quantentheorie*. Vieweg, Braunschweig (1983)
- [79] L. Graham, *Dialektischer Materialismus und Naturwissenschaften in der UdSSR*. Fischer, Frankfurt a. M. (1974); G.A. Wetter, *Philosophie und Naturwissenschaft in der Sowjetunion*. Rowohlt, Hamburg (1958)
- [80] D. Joravsky, *Soviet Marxism and Natural Science, 1971-1932*. Verlag. New York (1961); S. Tagliagambe, *Scienza e Marxismo in URSS*. Loescher, Torino (1979); *Scienza, filosofia, politica in URSS, 1924-1939*. Feltrinelli, Milano (1978)
- [81] V.I. Lenin, *Werke Bd. 14, Materialismus und Empiriokritizismus* (1909). Dietz, Berlin (1962).
- [82] Inheritance "Erich Hückel", Staatsbibliothek zu Berlin, Stiftung Preussischer Kulturbesitz, Collections of Manuscripts, Box 6/5.25, Letter to H. Hartmann of 24.2.1940
- [83] O. Schmidt, *Z. Elektrochem. Angew. Phys. Chem.* 42 (1936) 175
- [84] Nikolaj Sokolov, Moscow 6.4.1998. Also he reported that Zhukovitskij gave informations several years later against the Physicist Levin who disappeared in the GULag for ten years.
- [85] Per Wandzeitung wurde in allen größeren Institutionen Nachrichten verbreitet, die die Mitarbeiter betrafen. Sie wurde unter der Leitung des zuständigen Parteisekretariats – im Karpov-Institut also von Zhukovitskij –, hergestellt.
- [86] Tatjevskij, Moscow 28.4.1998
- [87] O. Chlewnjuk, *Das Politbüro. Mechanismen der Macht in der Sowjetunion der dreißiger Jahre*. Hamburger Ed., Hamburg (1998), S. 258.
- [88] G. von Rauch, *Geschichte der Sowjetunion*. Kröner, Stuttgart (1990)
- [89] W. Leonhard, *Die Revolution entläßt ihre Kinder*. Ullstein, Frankfurt a. M.(1974)
- [90] A. I. Vaksberg, *Gnadenlos. Andrej Wyschinskij - Mörder im Dienste Stalins*. Lübbe, Bergisch Gladbach (1991); A. Waksberg, *Die Verfolgten Stalins. Aus den Verliesen des KGB*. Rowohlt, Reinbek (1993)
- [91] Der Brief befindet sich im Archiv des Sohnes von Hans Hellmann
- [92] W. Röder, *Sonderfahndungsliste UdSSR. Geheim! Mit Faksimile*. Verlag für zeitgeschichtliche Dokumente und Curiosa, Erlangen (1975, 1977); *Exilforschung* 8
- [93] NKVD-Akte 'Hans Hellmann', 9.3.-29.5.1938, deutsche Übersetzung von S. R. Arnold im 'Hellmann-Archive Siegen'. Über den dort erwähnten Polen Rotseig/Rudtsaik ist nicht weiteres bekannt. Am 6.4.1957 haben Akademiemitglied Igor Vassiljevich Betranov und Gregorj Davidovich Ljubarskij aus dem Karpov-Institut positive Aussagen über Hellmann zu Protokoll gegeben.
- [94] Private information by Helga Rapley nee Munkelt (Nice of Hellmann) on sayings by her grandmother (mother of Hellmann) during the war, 15.12.1999
- [95] See end of section 2
- [96] Personal communications by M.A. Kovner, Levine and N. Sokolov on Nov. 30, 1999
- [97] J.I. Musher, *Amer. J. Phys.* 1966, 34: 267 – 268. See especially Note 4.
- [98] Richard Bader
- [99] Roald Hoffmann