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The Periodic Law and Progress in the Study of the Structure of Matter†

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A survey is made of the diverse achievements of Soviet scientists, rising to one of the founders of Russian chemistry—the genius D.I.Mendeleev and his greatest work—the periodic law, which has exerted an immense influence on the development of physics and chemistry at all four conceptual levels in the structure of matter—elementary particles, nuclei, atoms, and molecules. Consideration is given to the fundamental contribution made by Soviet scientists to predicting, discovering, and studying new isotopes and new types of radioactivity, to synthesising new transuranic elements and establishing their valency states (sometimes completely unexpected), and to founding the chemistry of "new atoms", in which proton and electron have been replaced by other elementary particles.

The principal modern methods for studying the structure of matter are based on the recording of hyperfine interactions between electrons and nuclei, electrons of outer and inner shells—i.e. essentially interactions between periodic and monotonic functions of the atomic numbers of the chemical elements. Soviet scientists both discovered the hyperfine interactions and made the most important contribution to their chemical utilisation (the discovery of electron spin resonance, the introduction of e.s.r. and γ-resonance spectroscopy into chemistry, the widespread application of nuclear magnetic resonance to chemistry, the establishment of photoelectronic spectroscopy in the ultraviolet and of accurate X-ray chemical spectroscopy, etc.).

The work of Soviet theoretical chemists in basing the periodicity in the properties of chemical elements on the molecular orbital method is reported, and illustrates how the periodic law preserves its fertility even at the modern quantum-mechanical level of attacking the problem of chemical bonds.

A list of 157 references is included.

The emergence and growth of chemical sciences in our country are indissolubly linked with three great names—M. V. Lomonosov, A. M. Butlerov, and D. I. Mendeleev—which we cannot fail to remember on the anniversary of our Academy. Each of these giants left an indelible mark in the history of science. Among the three, Mendeleev received the fullest recognition during his lifetime. More than 130 honorary titles and diplomas were conferred on him by Russian and foreign scientific societies, universities, and academies. But with all the brilliance of the confirmations of Mendeleev's chief creation—the periodic law—during his lifetime, its immense significance was disclosed still more fully by his successors. Mendeleev's feeling that "... the future will not threaten the periodic law with destruction but will only promise a superstructure and further development..." was realised[1].

For a long time a kind of hierarchy of the natural sciences—mathematics, physics, chemistry, biology—has been established, in which a "senior" science enriches a "junior" science with methods and concepts, thus stimulating its development. The periodic law was a brilliant example of the reverse relation in this hierarchy—an enormous and ramified influence of a chemical discovery on the development of physics.

Rutherford's discovery of the atomic nucleus and Moseley's investigation of X-ray spectra revealed the physical meaning of the serial number of an element in Mendeleev's system as the positive charge on its nucleus. Bohr's theory linked the planetary model of an atom with

† This paper is an expanded text of a lecture at the 250th Anniversary General Meeting of the USSR Academy of Sciences.

the quantum theory, gave a theoretical interpretation of the origin of periodicity in the chemical properties of elements, and enabled the structure of the sixth period in Mendeleev's system and the properties of the then unknown hafnium and rhenium to be predicted. But another consequence of comparing the periodic system with the quantum theory—Pauli's "exclusion principle" formulated in 1925—acquired a special and immeasurable importance. A path could be traced from Mendeleev through the Pauli principle to the Fermi-Dirac statistics and further to the theory of the valency bond, to the theory of atomic nuclei and universal weak interaction, of metals and semiconductors, superconductivity and superfluidity.

Mendeleev's law—or at least his method of systematisation and periodisation of the properties of known materials and extrapolation to new, as yet undiscovered materials—has found and finds wide application at all four levels (elementary particles, nuclei, atoms, molecules) in the science of the structure of matter. All the achievements in revealing a system in what was till recently chaos provide a guarantee of a deeper insight in the future. How clearly the great Mendeleev understood this is evident even from such remarkable words of his: "It can readily be supposed—but cannot yet be proved—that the atoms of elements are composite materials formed by the addition of several still smaller parts, that what we term indivisible (the atom) is indivisible only by ordinary chemical forces, as particles are indivisible under ordinary conditions by physical forces ... Such a view is evidently supported by the periodic relation I have formulated between properties and weight ..."[2].

The present Review will be concerned mainly with the most recent achievements of scientists—especially of Soviet scientists—in studying the structure of matter at the atomic and molecular levels, i.e. chemical structure. But first we must refer to elementary particles, especially to nuclei.

Recent decades have been marked not only by the discovery of a multitude of new elementary particles but also by the first major successes in their systematisation and the prediction of new particles on this basis. The author of the first systematic account of elementary particles, based on the introduction of a new (strangeness) quantum number and on application of the concepts of group theory, the American Nobel prizewinner Gell-Mann, makes a direct reference to the analogy between his work and Mendeleev's discovery of regularities in the properties of the chemical elements. He suggests that the system of particles will lead to a theory explaining their interactions, as the Pauli principle and quantum mechanics arose to explain the regularities and properties of atomic systems found by Mendeleev.

A still closer and still fuller analogy exists between the classification of the elements and the generally accepted classification of atomic nuclei based on the concept of the presence of many neutron and proton shells. This shell model of the nucleus led to the discovery of such an extremely important property of nuclear forces as their well developed dependence on the relative orientation of the spin and the orbital moment of the nucleons (neutrons and protons). Nevertheless, the creation and development of the shell model of the nucleus resulted from advances in the study of radioactivity, in particular the isomerism of artificial radioactive isotopes discovered in the USSR by Kurchatov and his coworkers in 1935.[3]

The fundamental contribution by Soviet scientists to the investigation of radioactivity—the spontaneous transmutation of chemical elements—can be illustrated by Fig. 1, which represents diagrammatically five main elementary types of radioactivity either already observed or predicted. Only two of them—α- and β-disintegration—were known by the end of the nineteenth or the beginning of the twentieth century. The third type—spontaneous fission—was discovered in 1940 in the USSR by Petrzhak and Flerov[4], at that time young students of V. G. Khlopin and I. V. Kurchatov. The fourth type—proton radioactivity—was suggested long ago by Rutherford, but was predicted from modern theories only in the 1950s by Soviet scientists[5-7], and observed experimentally only in 1970 in the cobalt-53m isomer[8]. The fifth and final type—two-proton radioactivity—was predicted in the USSR in 1960[6,9] and has not yet been observed experimentally. An interesting and expected feature of many dozens of nuclei having an even number of protons—the ability to emit a pair of protons together, but not single protons—is due to the pairing of protons having opposite spins, and has its chemical analogue in the formation of coordinate bonds, in which a single atom supplies the pair of electrons.

The coupling of the pairing effect, which is characteristic of all particles having semi-integral spins (electrons, protons, neutrons, etc., to which the general name *fermions* is given), with the presence of a potential barrier around the nucleus even with neutral particles (in this case a purely centrifugal barrier) leads to the possibility,

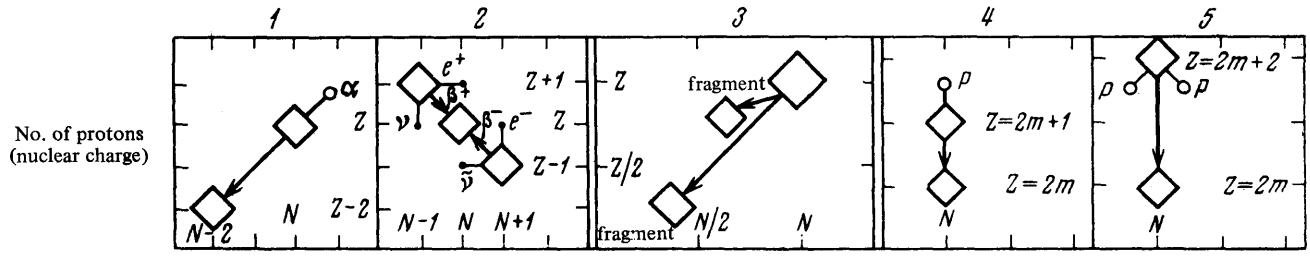


Figure 1. Schemes illustrating the five main types of radioactive disintegration of nuclei—spontaneous transmutation of chemical elements (e^- = electron; e^+ = positron; ν = neutrino; $\tilde{\nu}$ = antineutrino): 1) α-disintegration; 2) β-disintegration (β^-, β^+, and electron capture); 3) spontaneous fission; 4) proton disintegration; 5) two-proton disintegration.

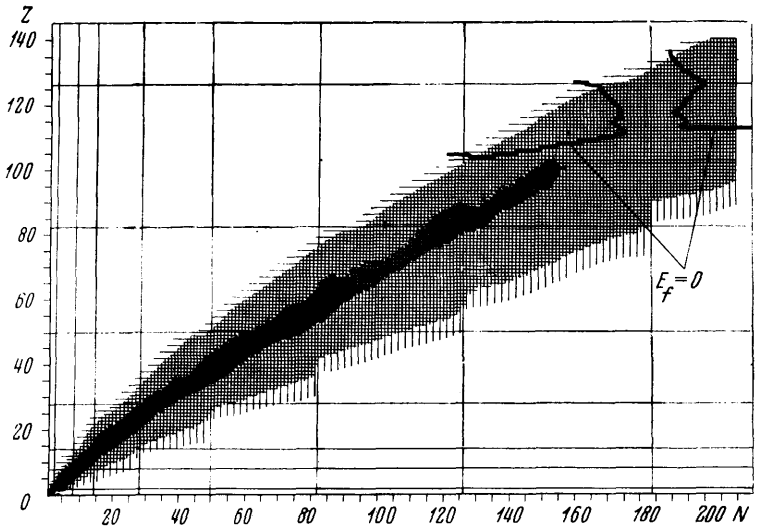


Figure 2. Region of stable and radioactive isotopes known at the present time (Z = No. of protons (atomic No.); N = No. of neutrons). The upper and lower boundaries are determined by the predicted instability for ejection of protons and neutrons respectively. The boundary of a possible "isthmus" of stability to spontaneous fission in the vicinity of $N = 184$ and $Z = 126$, 114 is indicated in the upper right-hand corner. In the absence of shell effects, spontaneous fission would have given a straight horizontal stability boundary near $Z \simeq 110$–112.

recently demonstrated theoretically, of the appearance of a sixth elementary type of radioactive disintegration of nuclei—two-neutron radioactivity, or the emission of a pair of neutrons by long-lived isomeric nuclei[9].

A few two-stage radioactive processes are known or have been predicted, in which the first step is some variant of β-disintegration, which is almost instantaneously followed by escape from an intermediate nucleus of some other particle (excited by part of the energy of β-disintegration) or by its fission. Such processes and the particles emitted in them are said to be *delayed*, the "delay" being due here to the sluggishness of the initial β-disintegration—i.e. not to the disintegration but to the formation of the excited nucleus.

Only delayed α-particles and neutrons were known before the Soviet work. The emission of delayed protons was discovered in the laboratory of G. N. Flerov at Dubna in 1962[10]. Another series of studies showed that the probability of fission of several transuranic nuclei was far higher than that expected from theoretical considerations, which was explained by the delayed fission of uranium and plutonium nuclei produced from neptunium and americium, as a result of slow electron capture from inner shells[11]. Theoretical analysis by Leningrad scientists indicated that tritium and helium-3 nuclei could also be emitted as delayed particles[12].

At the present time around 2000 isotopes of 105 chemical elements are known, of which only 15% are stable isotopes. However, systematisation of the bonding energies of nucleons in nuclei indicates the possibility of detecting almost 4000 more radioactive isotopes with a marked deficiency or a marked excess of neutrons in the nuclei. Fig. 2 shows clearly the relative regions of already known and not yet discovered isotopes. And the question of new isotopes involves not only their number: fundamentally new properties and phenomena await study.

The present stage of research on neutron-deficient and neutron-excess isotopes began in 1959–1960, when Soviet scientists[13,14], in particular Zel'dovich, proposed ways of determining the limits of stability of nuclei based on the shell theory of the nucleus and one of the main properties of nuclear forces—their independence of electric charges—since when dozens of new isotopes even of the lightest elements have been found, and their properties have shown excellent agreement with prediction. An extremely interesting example is the superheavy helium-8, which has double the weight of ordinary helium[15]. The prediction and detection of this isotope by Soviet scientists were marked by a discovery diploma[15]. Helium-8 is a kind of record-holder among atomic nuclei, in which each proton is associated with three neutrons. As a result of three successive radioactive transformations—two β-disintegrations and one α-disintegration (Fig. 3)—each atom of superheavy helium is converted into two atoms of ordinary helium, so that an aerostat filled with helium-8 inflated spontaneously to twice its volume in fractions of a second, without change in the chemical composition of the gas filling it.

In the search for new radioactive isotopes the synthesis of new transuranic elements acquired the widest popularity for understandable reasons, and greatly extended the limits of the Mendeleev periodic system. The first transuranic element (neptunium) was synthesised in 1940 and a fundamental contribution to extending the Mendeleev system was

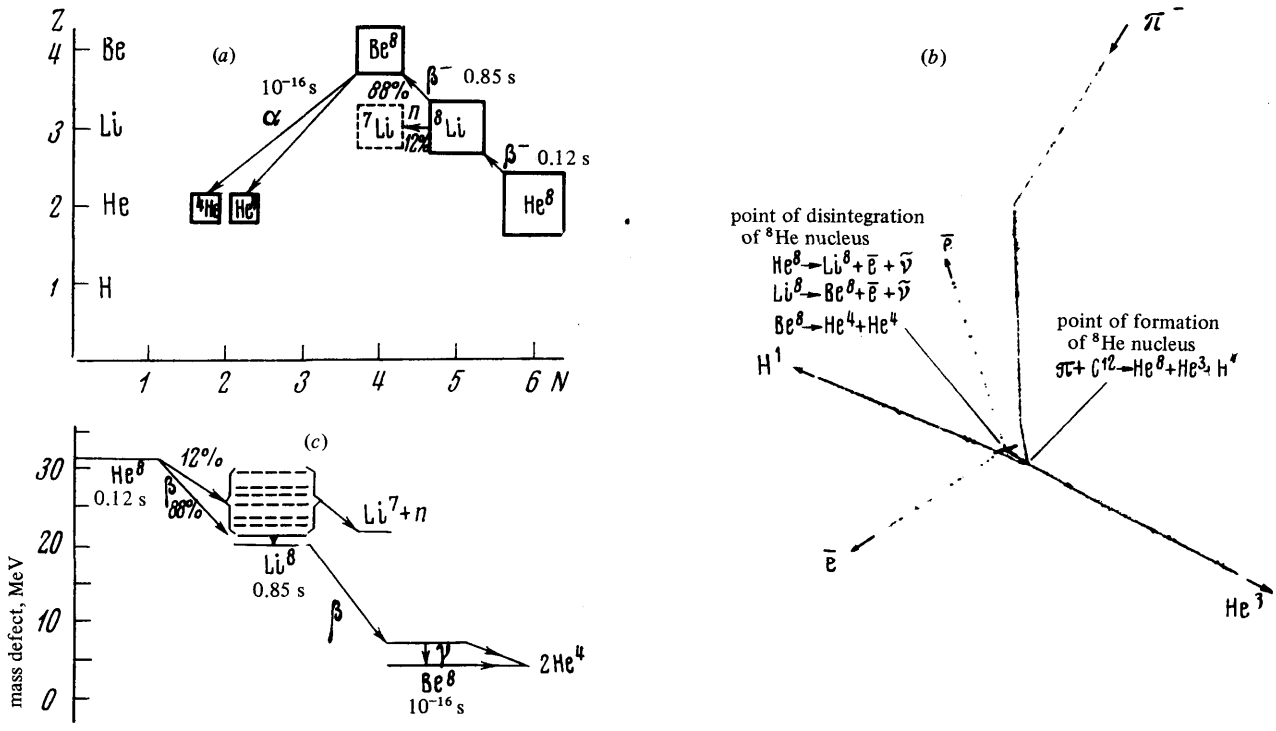


Figure 3. *a*) Illustration of disintegration path of helium-8 nuclei; *o*) pattern of formation of helium-8 nuclei by the bombardment of photographic emulsions with π-mesons ($\pi^- + {}^{12}C \rightarrow {}^1H + {}^3He + {}^8He$) and subsequent disintegration of helium-8 (obtained in the synchrocyclotron in the Laboratory of Nuclear Problems of the Joint Institute of Nuclear Research at Dubna); *c*) scheme of disintegration ($^8He \rightarrow {}^8Li \rightarrow {}^8Be \rightarrow 2{}^4He$).

made by a group of scientists headed by G. T. Seaborg at the Radiation Laboratory in Berkeley (U.S.A.) During 1941–1945 these workers obtained by means of accelerators, nuclear reactors, and nuclear explosions, eight new elements—from plutonium to element No. 101—the last of which they named *mendelevium* "... as a token in recognition of the priority of the great Russian chemist Dmitrii Mendeleev, who was the first to use the periodic system of the elements to predict the chemical properties of then undiscovered elements. This principle is the key to the discovery of almost all the transuranic elements"[16]. In 1958 scientists from Berkeley announced that they had obtained element 102 and in 1961 element 103, which they named respectively *nobelium* and *lawrencium*[17–19].

An enormous contribution to the synthesis and study of transuranium elements has since been made by Flerov's laboratory in Dubna. In 1963 and subsequent years Flerov and his coworkers obtained for the first time many isotopes of elements 102 and 103, which compelled them to revise the mass numbers previously assigned in Berkeley to the isotopes of these elements[20–23]. In 1964 the Dubna scientists achieved the remarkable success of obtaining the first isotope of the new element No. 104, named "kurchatovium Ku".[24] In February 1971 the synthesis was announced in Dubna of the next element 105, for which the name "nielsbohrium Ns" was proposed[25]. Several other isotopes of kurchatovium and of element 105 have since been synthesised in Berkeley.

Some idea of the latest situation is given by Fig. 4, in which are indicated all isotopes of the four newest elements known at the present time and those isotopes of elements 102 and 103 for which the presently accepted characteristics were first established in Dubna. Special emphasis is given to the isotopes discovered there of elements 104 and 105, which were incorporated by Soviet scientists into the Mendeleev system‡.

With regard to the main interest of chemists in the new elements—in their chemical properties—controversies have now continued for nearly thirty years on Seaborg's actinide theory, according to which actinium is followed by completion of a shell of fourteen 5*f* electrons in the elements from thorium to No. 103, analogous to the filling of the 4*f* shell in the rare-earth elements. A tendency sometimes develops to regard the periodic system as analogous not to a geographical atlas but to a plan which must indicate every street and every house, and to see any distinction between actinides and lanthanides as the overthrow of the actinide theory.

Nevertheless, the actual properties of elements in chemical compounds, the greater or lesser stability of their different valency states, are influenced by extremely

‡ In July 1974 the Dubna group announced the synthesis of new isotopes of kurchatovium (mass numbers 255 and 256) and the first isotope of element 106 (apparently A = 259).[25a]

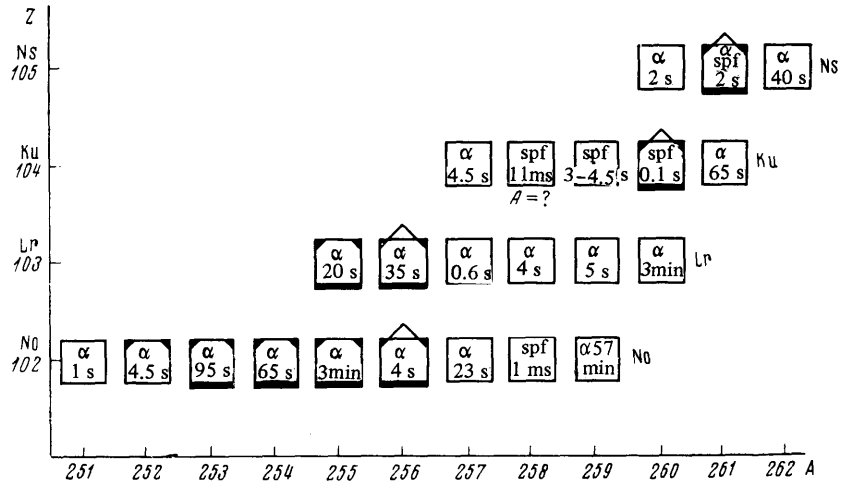


Figure 4. Isotopes of elements 102–105. The shaded corners and underlining denote those isotopes for which the presently accepted characteristics were first established at Dubna in the USSR. The triangles above the boxes indicate the first isotopes of each element, whose properties have not since been revised. The boxes contain the type of disintegration (spf = spontaneous fission) and the half-lives.

diverse factors. The problem can hardly be solved by model calculations. Even calculation of the energetics of the electron configurations of the free atoms and ions requires complicated programmes and high-speed electronic computers (as an illustration, it was thus established that the electron configuration $7s^27p$ for a free lawrencium atom was ~ 0.5 eV more advantageous, because of relativistic effects and spin-orbit splitting, than the lutetium-like configuration $6d7s^2$). No systematic molecular-orbital calculations have yet been made even for isolated molecules of lanthanide and actinide compounds. The same applies to real solutions and solid compounds, where the solvation energy as well as interionic and intermolecular interactions must also be taken into account, and with radioelements also the various effects of autoradiolysis. Here the chemist has the final say: comprehensive chemical investigations would prepare the ground for future calculations, and any new, especially unexpected facts lay the foundations for future general theoretical constructions.

For this reason it is difficult to overestimate the value of research on the chemistry of transuranium elements made during the past seven or eight years under the general direction of V. I. Spitsyn in the Institute of Physical Chemistry of the USSR Academy of Sciences. This led to the discovery of extreme valency states—septivalent neptunium, plutonium[26-29], and americium[30], bivalent californium, einsteinium[31], and fermium[32], and univalent mendelevium[33].

The septivalent states of the three actinides could be achieved by oxidation only in alkaline media, in which neptunium could be oxidised by more than twenty oxidants, and plutonium by more than ten, including ozone, persulphate, hypobromite, and the radical-ion $O^{\cdot-}$, the last being formed by the radiolysis of aqueous alkalis. It was most difficult to obtain septivalent americium: this required the radiolysis of alkaline solutions of americium(VI) cooled almost to 0°C and supersaturated with nitrous oxide, which is an acceptor of the strong reductant—the hydrated electron—produced by radiolysis. Around twenty solid compounds of septivalent neptunium and plutonium have been obtained—mainly perneptunates and perplutonates of alkali and alkaline-earth metals.

Fermium and mendelevium were reduced to the lowest valencies by the action of magnesium in aqueous–ethanolic solutions of chlorides of inert carriers. The lowest valency state of mendelevium was detected with only a few hundred atoms of the mendelevium-256 isotope (half-life 1.5 h) available.

The experimental valency states found by Soviet scientists for the above five actinides are indicated by crosses in Fig. 5, which includes all such states known for lanthanides and actinides (the most stable states are denoted by small squares). Fig. 5 shows both properties common to the two groups and their differences, which are due to the close approach in bonding energy of the ns, np, $(n-1)d$, and $(n-2)f$ electrons that is characteristic of the heavier elements. The results of these investigations by Spitsyn and his coworkers indicate a certain affinity between the far actinides ($Z \geqslant 98$) and the transition d-elements, as well as the possibility of discovering octovalent plutonium, quinque- and sexi-valent curium, and quinquevalent berkelium.

Fig. 5 includes also results obtained at Dubna in the USSR by a group of Soviet and Czechoslovak radiochemists under the general direction of Zvara[34-37]. They developed a method, of record rapidity and sensitivity, for establishing the chemical nature of new elements from the volatility of their anhydrous halides. In 1966 this method was used to demonstrate that kurchatovium and hafnium chlorides were closely similar in volatility, and significantly less volatile than the chlorides of actinides[34]. This decisive experiment, which proved that element 104 is already a member of the titanium subgroup of Group IV, and that element 103 sees the completion of the fourteen-electron $5f$ shell, in conformity with the actinide theory,

needed only 16 atoms of kurchatovium. The properties of this element were subsequently confirmed and refined by isolating and recording the radioactive decay of 60 of its atoms[35]. Furthermore, it was shown that nobelium and lawrencium are at most tervalent in their chlorides[35,36]. An outstanding new achievement was the observation that nielsbohrium chloride is more volatile than hafnium tetrachloride but less volatile than niobium pentachloride, as was to be expected for quinquevalent ekatantalum[37]. It must be emphasised that the experiments were made on isotopes of kurchatovium and nielsbohrium whose lifetimes did not exceed a few seconds.

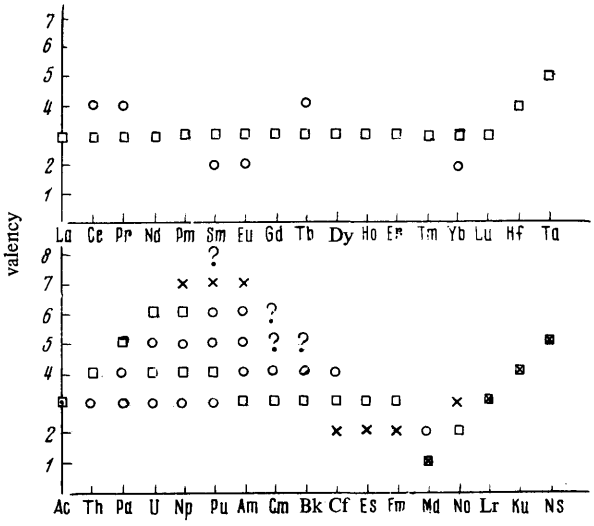


Figure 5. Valency states of lanthanides and actinides (as well as hafnium, kurchatovium, tantalum, and nielsbohrium). The most stable states are indicated by squares, and states first detected in the USSR by crosses (Np, Pu, Am, Cf, Es, Fm, and Md at the Institute of Physical Chemistry of the USSR Academy of Sciences, and No, Lr, Ku, and Ns at Dubna).

Advances in the synthesis and in the study of the properties of the far transuranium elements have enhanced the interest taken in the problem of the limits to which the periodic system can be extended. Only a decade ago it was supposed that spontaneous fission restricts the possibilities of synthesising elements 110–112. However, calculations by Soviet and foreign theoretical nuclear physicists[38–40] indicated that significant stabilisation of nuclei might result from the filling of nuclear shells containing 114, 126, and 164 protons, 184 and 258 neutrons. As a result the "isthmus of stability" shown in Fig. 2 may well appear, and contain many isotopes of elements in the vicinity of positions 114, 126, and even 164 in the Mendeleev system.

With regard to the chemical properties to be expected of these elements, data on the presently known elements and their extrapolation yield the sequence of electron shells depicted in Fig. 6. Each period is represented here by cells containing the symbols of the electron shells filled in the given period: i.e. each cell contains 2, 6, 10, 14, or 18 elements. Element 114 terminates the seventh period, element 164 completes the eighth period, and both are analogues of lead. Element 126 will occur in a new group of 18 elements—"octadecanides", apparently resembling actinium and in whose atoms the 5*g* shell will be completed—forming part of the 50-element eighth period[41–42]. The hypothetical eighth period is completed in Fig. 6 by element 168, and the ninth period by element 218.

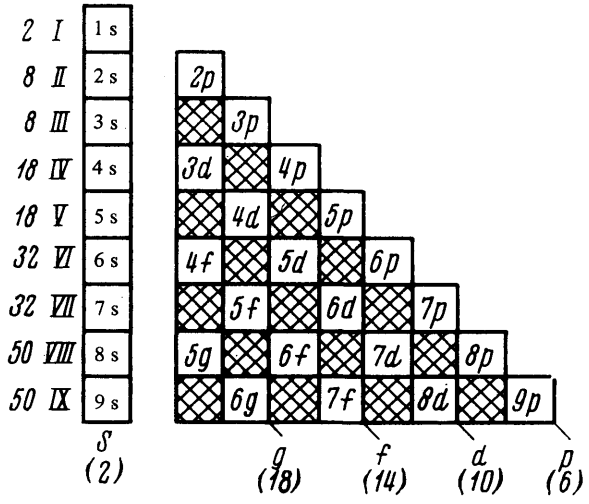


Figure 6. Diagram of sequence in which electron shells are filled in the periodic system. The total number of elements in the period indicated by the Roman numeral (which equals the serial number of the *s*-shell) is listed on the left-hand side. The total numbers of electrons in the various complete shells are given below the diagram.

Quite a number of attempts have been made during recent years to find in Nature or to obtain in accelerators some superheavy elements, but this has not yet been done with sufficient certainty. However, the links between the chemistry and the physics of elementary particles which have appeared recently have opened up completely new prospects for enriching and expanding our ideas on chemical elements. This refers to the numerous examples of so called "new atoms", in which the proton has been replaced by a different positive particle, or the electron by a different negative particle[43]. The possibility of replacing a proton by a lighter positive particle implies that ordinary hydrogen (protium) will cease to be the lightest occupant of the first position in the Mendeleev system. For example, we are now acquainted with kaonium, pionium, and muonium, in which the proton has been replaced respectively by a κ^+, π^+, and a μ^+ meson, and whose atoms are lighter by factors 2, 7, and 9. The lifetimes of these atoms are determined by the decay of the mesons and lie in the range 10^{-8}—10^{-6} s. The lightest conceivable isotope of hydrogen is positronium Ps, whose atom comprises a positron and an electron, and is lighter than hydrogen by a factor of 920. Because a positron has the same mass as an electron, positronium is the only atom completely devoid of a heavy nucleus. Apart from

its extraordinarily small mass, positronium differs from ordinary radioactive hydrogen (tritium) in the most important fact that all the characteristics of its loss by mutual annihilation of the positron and the electron—lifetime, number of γ-quanta emitted on annihilation, their energy and angle of divergence—depend on the properties of the surrounding medium, which permits a completely fresh investigation of these properties. The extremely short lifetime of positronium (10^{-10}–10^{-7} s) hinders its accumulation in concentrations exceeding a few atoms per cubic centimetre, so that none of the classical methods of chemistry can be used to study the reactions of positronium. This can be done only by nuclear methods, which enable the formation and destruction of every single positronium atom to be observed by recording the accompanying γ-quanta. Combining such methods with wide variation in the external conditions—composition of medium, concentrations, temperature, pressure, etc.—has enabled comprehensive quantitative investigations of all types of chemical reactions undergone by positronium to be made in the Institute of Chemical Physics of the USSR Academy of Sciences during the past twelve years[43–45]. Examples are given in Table 1 of oxidation, donor–acceptor interaction, substitution, addition, and conversion. Thus, for the first time in the history of radiochemistry, a detailed study has been made of the chemistry, including the kinetics and the mechanism of the reactions, of atoms which last at most 10^{-7} s.

Table 1. Examples of chemical reactions of positronium.

Type	Example	Method	Medium
Oxidation	$Ps + Fe^{3+} \rightarrow e^+ + Fe^{2+}$	time, angle	aqueous solutions
Donor–acceptor interaction	$Ps + M(C^+:) \rightleftarrows PsM$ carbonium ion	time	organic solutions
Substitution	$Ps + Cl_2 \rightarrow PsCl + Cl$	time, angle	gases, organic solutions
Addition	$Ps + (CF_3)_2NO \rightarrow (CF_3)_2NOPs$	time, angle	gases, solutions, solid phase
Ortho–para-conversion	$o\text{-}Ps + NO \rightarrow p\text{-}Ps + NO$ ($\uparrow\uparrow$ $\downarrow$ $\uparrow\downarrow$ $\uparrow$)	time, angle	gases, solutions
"Mixed" interaction (conversion or addition)	$o\text{-}Ps + NO_2 \rightarrow PsNO_2$, $p\text{-}Ps + NO_2$ ($\uparrow\uparrow$ $\downarrow$ $\uparrow\downarrow$ $\uparrow$)	time, angle	gases, aqueous and organic solutions

Despite the intrinsic interest of the chemistry of positronium, results obtained by the new positronium method for chemistry as a whole are of greater significance. For example, by using as standard the extremely short "proper" lifetime of positronium (with respect to annihilation), it was possible to measure the rates of several ultra-rapid chemical reactions occurring within fractions of a nanosecond and lifetimes of intermediate products of the order of picoseconds. Varying the temperature and the composition of the solvent in which the reactions of positronium were observed yielded a general technique for delimiting kinetic and diffusion régimes in the kinetics of liquid-phase reactions. Comparison of the rates of various reactions of hydrogen and positronium atoms led to a general conclusion on the mechanism of electron transfer in oxidation by ions of variable valency in solution. Observations on the reactions of positronium with a carbonium ion in different organic structures made it possible to determine the electronic conductance of various groups relative to that of the benzene ring.

Thus the chemistry of positronium has already passed the stage of "fitting" its possibilities to known facts and has entered the second, main stage, when it supplies new information of value to chemistry. The chemistry of other new atoms, sometimes termed in general *mesochemistry*, is still at the first stage, although the results already obtained are extremely promising. Pioneering work on mesochemistry has been done with the synchrocyclotron at the Laboratory of Nuclear Problems (directed by V. P. Dzhelepov) of the Joint Institute of Nuclear Research in Dubna, by the staff of this laboratory and several others, including academic institutes[46–67].

Systematic research on the physicochemical interactions of the hydrogen-like atom of muonium was undertaken at the Institute of Theoretical and Experimental Physics of the USSR State Atomic Energy Commission[43,46–50]. A method was proposed and developed[51–53] for determining the absolute rate constants of the chemical reactions of muonium with organic and inorganic compounds, the mechanism of these reactions was investigated, and quantitative dependences of reactivity on molecular structure were obtained. Known nuclear physical constants of the μ^+ meson and muonium were used as independent time standards, which permitted study of the behaviour of single muonium atoms during times of 10^{-9}–10^{-5} s. Conversion to hydrogen of results for the reactions of muonium in several cases provided more accurate characterisation of the reaction rate for hydrogen atoms themselves than did the corresponding direct experiments. The temperature dependence of the reactivity of muonium was examined, and activation energies of its reaction were determined. A sharp jump in polarisation of the μ^+ meson was revealed for the water–ice phase transition, associated with formation of a closed coordinated system of hydrogen bonds in the ice crystal.

The presence of Larmor precession of triplet muonium was first shown in chemically inert condensed media, and the energy of hyperfine splitting in the muonium atom was determined as a function of the periodic lattice potential of several materials, including semiconductors. Spin-exchange interactions of muonium in solutions of paramagnetic ions have been studied, and a close analogy was shown with results obtained by nuclear magnetic resonance but with substantial broadening of the range of measurements with respect to concentrations and spin–spin relaxation times.

The two-frequency spin precession of the μ^+ meson in the muonium atom, resulting from a quadratic Zeeman effect in the ground-state levels of muonium, was discovered[54] at the Kurchatov Institute of Atomic Energy of the USSR State Atomic Energy Commission. The two-frequency precession was used to study the properties of muonium introduced into the crystalline matrix of several materials. A method for studying diffusion of the μ^+ meson and muonium in a solid was based on the dependence of the interaction between the magnetic moment of the μ^+ meson and those of the nuclei of the medium on the rate of diffusion of the meson in the crystal lattice[55,56]. Spin relaxation of the μ^+ meson caused by dipole–dipole interactions was noted in metals and in light and heavy ice.

The interaction with matter of μ^- and π^- mesoatoms, in which one of the electrons has been replaced by a μ^- or π^- meson, is also of great interest[57-67]. Negatively charged mesons are slowed down in a medium, and ultimately trapped in atomic orbitals to form mesonic atoms and then, in a series of cascade transitions with emission of mesonic X-rays, reach the ground state in the inner K shell. Study of the characteristic X-ray emission spectrum, the lifetimes of the mesons, and their depolarisation enables the interaction of μ^- mesons with matter to be investigated. Observations on the chemical reactions of π^- mesons are based on comparing the specific pattern of their decay on interaction with free protons with the decay within any other π-mesonic atoms. Such work was begun more than ten years ago in the Laboratory of Nuclear Problems of the Joint Institute of Nuclear Research (by Prokoshkin and his coworkers[58,59]); recently the Institute of Chemical Physics of the USSR Academy of Sciences, the State Institute of Applied Chemistry, etc. have taken part in this work.

Since the radii of atomic orbitals are inversely proportional to the mass of the particles occupying them, this radius is minute—around 10^{-11} cm—for atoms of mesohydrogen in the ground state. It would seem that mesonic atoms should not be affected by other chemical bonds at distances of hundreds of mesoatomic dimensions in the molecule. Therefore the discovery of many relations for mesonic atoms which conform to the Mendeleev periodic dependence on atomic number Z was completely unexpected. Fig. 7 illustrates examples of such regularities for μ^-- and π^--mesonic atoms (given for π^- by the relation

where $W^{exp}_{Z_mH_n}$ is the experimental probability of the nuclear capture of π^- mesons by protons of hydrogen atoms). Such examples led to the so-called "model of large mesomolecules"[60-62] for the properties and transformations of molecules involving excited mesonic atoms, in which the meson is situated not in the ground state but in an orbital remote from the nucleus which has a principal quantum number n and hence a radius increased by a factor n^2, and reaches normal atomic dimensions. Fig. 7 shows that such orbitals are no longer mesoatomic but are mesomolecular. Observations of the formation and the transformations of large mesomolecules yield several conclusions on the properties of other valency bonds in these molecules and on the electronic effects of various functional groups. Furthermore, such observations enable a definite correlation to be established between mesochemical and radiation-chemical reactions and the rate constants of chemical reactions involving mesonic atoms and radicals to be determined.

We have already mentioned the four levels in the structure of matter, and have proceeded from particles through nuclei to atoms and molecules. But the highroad of modern research is based on the synthesis of ideas on

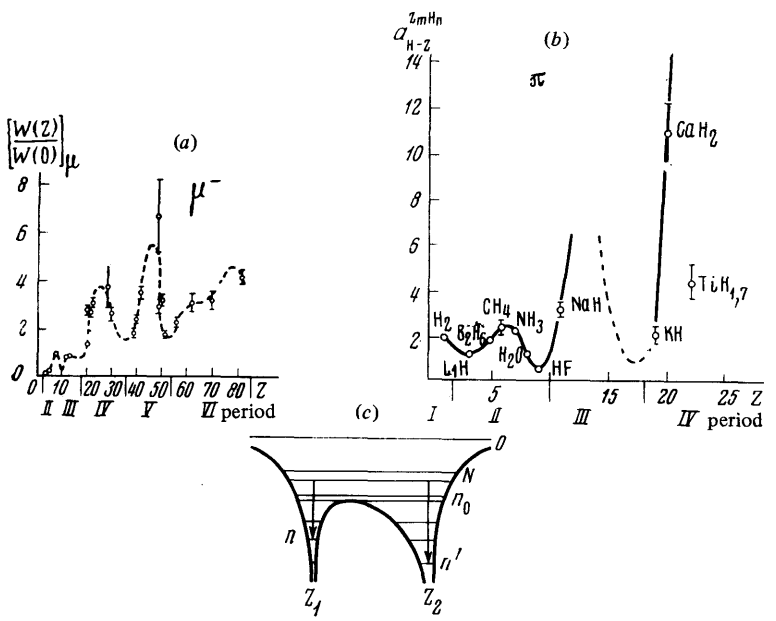


Figure 7. Examples of periodic dependence of certain mesoatomic reactions on atomic number of element Z: *a*) ratio of probabilities of atomic capture of μ^- mesons by element Z and by oxygen chemically combined with it in oxides Z_mO_n;[57] *b*) coefficients $a_{H\text{-}Z} = W(H)/W(Z)$ representing ratio of probabilities of capture of π-mesons by hydrogen and by element chemically combined with it in the saturated hydride Z_mH_n (aggregate of data from several Soviet and foreign papers); *c*) scheme of mesonic levels in diatomic "large mesomolecule" Z^1Z^2. Above n_0 are generalised mesomolecular levels, and below it are located mesoatomic levels Z^1 and Z^2.[60]

the structure of nuclei and electron shells, on the unity of the quantum-mechanical description of the properties of both.

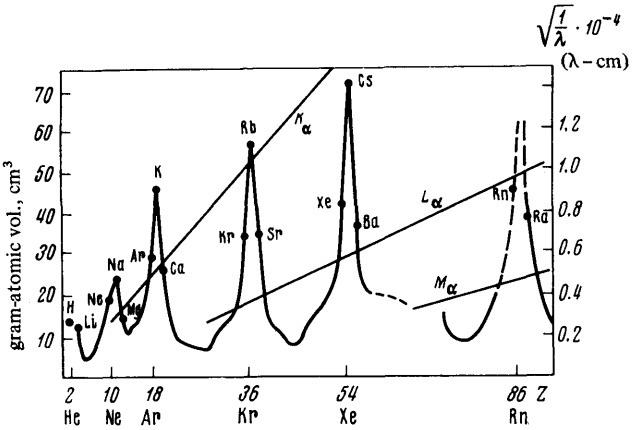


Figure 8. Typical examples of periodic dependence (of atomic volume) and linear dependence (of square root of wave-number of α-lines of K-, Z-, and M-series X-rays—Moseley's law) on atomic number Z of element.

The discovery and interpretation of Mendeleev's periodic law provided for chemistry and physics the two types of dependence of properties of the electron shells on the nuclear charge illustrated in Fig. 8. For the outer, valency shells we have a periodic relation, represented here by the atomic volumes. The relation of the inner, deep shells is a monotonic power dependence represented in Fig. 8 by Moseley's linear law.

The next contemporary stage, to whose establishment and development Soviet scientists have made an enormous contribution, entails the detection, examination, and utilisation in chemistry—and in all other natural sciences—of interactions between outer and inner electrons, outer electrons and nuclei, i.e. interrelations as it were between periodic and power functions of the atomic numbers of the elements (with the atomic numbers themselves as a particular case).

The first example of such interactions, now combined under the name *hyperfine interactions*, was discovered in 1928 by Terenin and Dobretsov[68], and independently by Schüler[69], as a result of accurate investigations on the optical spectra of sodium vapour. It was found that each of the two components of the yellow D-line was split only by 0.02 Å, and this splitting could be explained on the assumption that spins and magnetic moments were present not only in the electrons but also in the nuclei. In the above work, incidentally, Terenin and Dobretsov used for the first time atomic beams—a technique which has since been widely used in various resonance methods.

Table 2 lists the various forms of hyperfine interaction and methods involving their use. One of the main types is the interaction of the electric charges and the magnetic and quadrupole moments of nuclei with the charge of the s-electrons and the intramolecular magnetic and non-uniform electric fields. These hyperfine interactions are used in electron spin resonance (discovered by Zavoiskii[70,71] in 1944) and in other methods of microwave spectroscopy, in particular nuclear magnetic resonance and nuclear quadrupole resonance. Hyperfine interactions play a decisive role also in γ-resonance or Mössbauer spectroscopy, first placed in the service of chemistry by the work of Soviet scientists[72,73]. The hyperfine interaction energy involving valency electrons is in all cases many orders of magnitude smaller than even those of the weakest chemical bonds, and the dependence of this energy on the nuclear charge is represented by most insignificant periodic bumps, as it were, on the background of far stronger periodic or monotonic relations. Fig. 9 shows as example of this situation logarithmic plots of the periodic dependence on atomic number of the density of valency s-electrons in the region of the nucleus and the monotonic increase in total density of all s-electrons on the nuclei of elements from lithium to krypton.

Table 2. Hyperfine interactions and methods of use.

Type of interaction or dependence	Parameter and energy of interaction*	Experimental methods
Magnetic dipole (M1) interaction between nucleus and unpaired ("own" or "foreign") electrons	$\mu_{nucl}H \sim 10^{-6} - 10^{-4}$ eV	microwave spectroscopy—e.s.r., n.m.r.
Electric quadrupole (E2) interaction between nucleus and valency electrons or neighbouring ions	$eqQ \sim 10^{-7} - 10^{-6}$ eV	n.q.r. double resonances, spin echo, etc.
Coulombic (electrostatic—E0) shielding of nuclear charge by s-electrons	$\frac{V_{nucl}}{V} I_1 \sim 10^{-8} - 10^{-7}$ eV	Mössbauer
Coulombic (electrostatic—E0) shielding of charge of inner by outer electrons; dependence of energy of vacant levels on effective charge of atomic core	$\frac{V_{inner}}{V} I_{inner} \sim 0.1 - 10$ eV	X-ray electron and photoelectron spectroscopy or e.s.c.a.
Dependence of Coulombic energy of interaction of electrons with nuclei on nuclear mass (isotope effects in ionisation potentials)	$\frac{m}{M} \cdot \frac{\Delta M}{M} I \sim 10^{-6} - 10^{-2}$ eV	Accurate chemical X-ray spectroscopy, determination of effective charges on atoms
Dependence of energy of vibrational levels on nuclear mass (isotope effects in vibrational levels of molecules)	$\frac{\Delta M}{M} E_{vibr} \sim 10^{-4} - 10^{-3}$ eV	Accurate optical spectroscopy and laser methods for separating isotopes

* μ_{nucl} = magnetic moment of nucleus; H = intramolecular magnetic field on nucleus; e = charge of electron; q = gradient of intramolecular electric field; Q = quadrupole moment of nucleus; V_{nucl} = volume of nucleus; V = volume of atom; V_{inner} = volume of inner shell; I = ionisation potential (I_1 for first electron, I_{inner} for inner electron); m = mass of electron; M = mass of nucleus; ΔM = difference in mass between isotopes; E_{vibr} = energy of vibrational level.

Interaction between the electric charges of the outer and inner electron shells is apparent in changes (of fractions or even a few electron-volts) in the energy of electrons removed from the inner shells of the atoms, and it also leads to the appearance of a specific fine structure in the X-ray spectra. This forms the basis of the so called photoelectron spectroscopy, whose X-ray and ultraviolet forms were established by Siegbahn et al. in Sweden[74,75] and by Terenin et al. in the USSR[76], and also of precision chemical X-ray spectroscopy, founded by workers of the USSR Academy of Sciences at the Vernadskii Institute of Geochemistry and Analytical Chemistry, the Institute of the Mineralogy, Geochemistry, and Crystal Chemistry of the Rare Elements, the Kurnakov Institute of General and Inorganic Chemistry, and the Konstantinov Institute of Nuclear Physics[77-83].

Finally, the isotopic dependence of the vibrational energy levels and the ionisation potentials has recently found most interesting application for the laser separation of isotopes, which has been accomplished in the Institute of Spectroscopy of the USSR Academy of Sciences[84].

A few examples may be cited of the great successes achieved by Soviet scientists in the use of hyperfine interactions in various chemical problems. Some years after the discovery of electron spin resonance by Zavoiskii, and in the same place Kazan, the first observation of hyperfine structure in e.s.r. spectra was made by Kozyrev et al.[85] (and independently in England[86]), which ensured the successful application of the new method in chemistry[86]. Chemical e.s.r. spectroscopy owes its origin largely to Voevodskii[87], who made it a powerful weapon in structural kinetic investigations, in particular the observation of free radicals formed directly during irradiation of various substances, as well as in investigations on so called weak chemical interactions[88,89], whose energy is incomparably smaller than the usual thermal energy but close to the energy of hyperfine interactions. Such interactions are too weak to be observed by methods like optical spectroscopy, measurement of dipole moments, etc.; yet they often control a most important chemical phenomenon—the mutual influence of the reactivities of different functional groups distant from each other—and are apparent in differences (spatial or temporal) in the delocalisation of electrons in the molecules. The e.s.r. method made possible the direct observation of such delocalisation of electrons[90,91], attempts at which had been begun towards the end of the 1950s[90] on radical-anions of the type shown at the top of Fig. 10. But here the left-hand and right-hand rings are not equivalent, owing to the approach of a gegenion (e.g. Na^+, R^+) towards the negative charge, and this prevents delocalisation—"erosion" of the free valency and the negative charge between the two rings. Only quite recently has the exchange of electrons been demonstrated between two distant identical functional groups, in the stable nitroxide biradical shown in the middle of Fig. 10.[91] The e.s.r. spectrum of this biradical in various solvents is characterised by five (bottom right in Fig. 10)—not

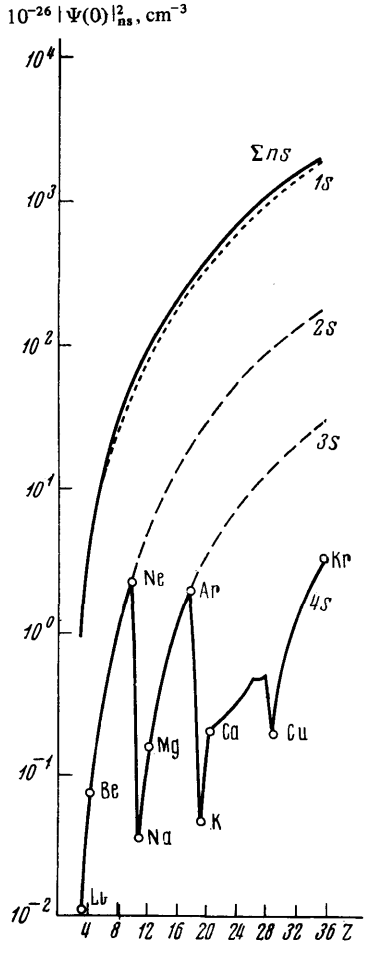


Figure 9. Dependence on atomic number Z of s-electron densities (all calculated per s-electron to a non-relativistic approximation): valency s-electrons $|\Psi(0)|^2_{ns}$ in region of nucleus (bottom full curve); 1s, 2s, and 3s densities (broken curves); total density of all s-electrons (upper full curve).

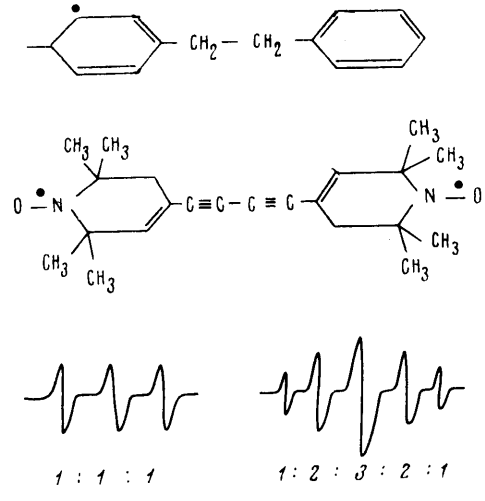


Figure 10. Illustration of e.s.r. investigation of the delocalisation of electrons in molecules: examples of test materials (radical and biradical) (above and centre); typical spectra corresponding to localisation (triplet) and delocalisation (quintet) of electrons in nitroxide biradical (below).[91]

three (bottom left)—hyperfine splitting components, which indicates that each of the unpaired electrons at once undergoes the same interaction with the two (its "own" and the "other") nitrogen-14 nuclei. The frequency of the effective exchange of position by the two electrons here exceeds 10^8–10^9 s^{-1}.

Among other interesting recent chemical applications of e.s.r. we may mention direct observations of the tunnel transfer of electrons in irradiated frozen alkalis at low temperatures, when the distance tunnelled is reckoned in tens of ångströms [92]. The method proved to be sensitive to extremely slow movements of paramagnetic labels, with linear speeds reaching 10^{-7} cm s^{-1} and diffusion coefficients reaching 10^{-17}–10^{-18} cm^2 s^{-1}. [93] It is difficult to overestimate the possibilities which such observations open up for physicochemical biology, the study of molecular kinesis phenomena§, in particular conformational transitions of biopolymer molecules, and various types of motion at molecular, supermolecular, and cellular levels. The e.s.r. method originated in experiments on a condensed phase, to which it was restricted for a long time. Subsequently, however, it found fairly wide application for the study of branched chain reactions in the gas phase [94,95] and from 1967—mainly in the work of Nalbandyan et al. [96–98] and because of the substantial improvement in the sensitivity of e.s.r. instruments—also in the investigation of degenerate branched gas-phase reactions, of particular theoretical and practical interest, such as the oxidation of hydrocarbons, when the concentration of active centres is far smaller.

Further prospects for studying the gas-phase and surface reactions of paramagnetic atoms and free radicals by means of hyperfine interactions are opened up by the maser kinetic method developed by Tal'roze and his coworkers [99,100]. Here, as in e.s.r., use is made of the magnetic hyperfine interaction between electron and nucleus, which in hydrogen atoms causes certain transitions between two hyperfine sublevels of the ground state of wavelength 21 cm. Interaction of a beam of hydrogen atoms from a hydrogen quantum generator (the maser) with various molecules leads to the observed relaxation of the inversion of hyperfine sublevels, so that excellent accuracy can be ensured in the determination of rate constants with around 10^4 improvement in sensitivity relative to e.s.r. in the gas phase.

At the present time about 50% of all e.s.r. spectrometers used in world science are concentrated in the Soviet Union. The widespread introduction of e.s.r. in industry—for rapid analysis or for the optimisation of several technical and in particular catalytic processes using paramagnetic ions of transition metals—promises to have a very considerable economic effect. A theoretical basis for such development may be provided by the comprehensive series of investigations made at the Vernadskii Institute of Geochemistry and Analytical Chemistry [101] on the application of e.s.r. to the study of complex formation by paramagnetic ions in solution. Portable e.s.r. spectrometers suitable for the above purposes have been suggested in the Institute of Chemical Physics [102].

Nuclear magnetic resonance has found extraordinarily wide use by Soviet chemists. Because of the thorough isolation of a system of nuclear magnetic moments from all other degrees of freedom, it is characteristic of this form of microwave spectroscopy that the exchange of energy between this system and the environment in a condensed phase is extraordinarily difficult. Nuclear magnetic spin–lattice relaxation times reach many hours in molecular crystals, and many minutes in pure organic liquids (about the same as the spin–spin relaxation time in liquids). However, the action of the various local fields is averaged out in liquids by Brownian motion, and in the solid phase by the superposition of specially selected external high-frequency fields. Hence under the usual experimental conditions, i.e. with external magnetic fields of $\sim 10^4$ G, when the energy of interaction of the nuclear magnetic moments with the field is of the order of 10^{-7} eV, while the characteristic frequency of precession of these moments $\nu \simeq 10^8$ Hz, n.m.r. lines can be obtained of width reaching $\Delta\nu \simeq 10^{-2}$ Hz. Although the relative width of the n.m.r. spectral lines $\Delta\nu/\nu \simeq 10^{-10}$ is several orders of magnitude larger than for the Mössbauer effect, the n.m.r. method has as yet no peers with respect to absolute line width ($\Delta\nu \simeq 10^{-2}$ Hz corresponds to $\Delta E \simeq 10^{-17}$ eV). Two factors—the chemical shift and indirect spin–spin interaction of nuclei—are responsible for the regular displacement, depending on the molecular structure of the medium, undergone by peaks of such record narrowness. The range of dimensionless chemical shifts varies from 2×10^{-5} for protons to $\sim 10^{-4}$–10^{-3} for heavy atoms. Spin–spin interaction constants vary in absolute value from zero to several kilohertz depending on the density of valency electrons in the region of the nucleus and on the degree of overlap of electrons in the chain of bonds at whose ends are situated the two atoms whose nuclear interaction is under investigation.

The contribution made by Soviet scientists to establishing the theoretical foundations of nuclear magnetic resonance is very great. Work in the Institute of Chemical Physics of the USSR Academy of Sciences, which has acquired a world-wide reputation [103], combined the concepts of a spin temperature and a reservoir of dipole–dipole interactions, and gave widely quoted equations describing the processes in a system of nuclear spins for any value of the saturating field. The Soviet book "Teoriya Yadernogo Magnitnogo Rezonansa" [104], which gave the first general theory of the magnetic shielding of nuclei, became a work of reference for n.m.r. specialists throughout the world.

Studies undertaken in the Institute of Organoelementary Compounds of the USSR Academy of Sciences provide the chief examples of the fundamental experimental results which we have obtained by means of nuclear magnetic resonance. Some time ago Nesmeyanov made a detailed analysis of the close relation between the chemistry of organoelementary compounds and the periodic law [105]. A clear recent confirmation of such a relation was the establishment [106] of periodicity in the shielding of carbon nuclei in cyclopentadienyl ligands of isostructural π-complexes of transition metals (shielding is maximal with the iron subgroup, as shown in Fig. 11). However, n.m.r. reveals far finer regularities. Electronic effects due to different substituents are widely discussed in chemistry, but what occurs at the point of bonding of substituents remained well hidden and was the subject of theoretical speculations, for the key (substituted) atom itself is usually not involved in the range of interactions for which the role of substituents is considered.

Fig. 12 shows the variation in shielding of the key carbon atom in a substituted aromatic system [107]. The effect of substituents on the key atom was found to be stronger in absolute value by factors of 10–10^2 than in the "strictly aromatic" part of the molecule, and furthermore, when the bond with the substituent was weakly polar (with alkyl

§ The term "moleculokinesis", meaning the functional motion of molecules, was introduced by V.A. Engel'gardt.

or methine groups), its sign was opposite to that to be expected from the electron-donor or electron-acceptor character of the substituent. With alternant aromatic systems this alternation of sign is considered also within the region of ring delocalisation of π-electrons; in non-alternant systems the reversed sign of the effect is characteristic only of the key atom. These facts give an experimental guideline for choosing an adequate quantum-chemical description of the electronic effects of weakly polar C-substituents. If, however, the bond between the key atom and the α-atom of the substituent is strongly polar, the carbon-13 n.m.r. chemical shifts vary in conformity with the usual views on the inductive effect of a substituent: i.e. alternation of the effect on the key carbon atom is now absent. This is clearly seen from the central portion of Fig. 12, which shows the variation of shielding and the parallel variation of the total electron density of corresponding carbon atoms in a cyclopentadienyl ligand of ferrocene with a carbonium ion as substituent. The lower part of Fig. 12 shows the superposition of effects which is characteristic of substituents of mixed type, e.g. formyl.

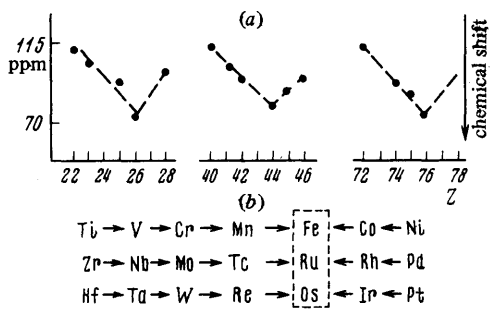


Figure 11. (*a*) Plots of variation in chemical shifts (ppm with respect to tetramethylsilane) of ^{13}C nuclei in n.m.r. spectra of unsubstituted ligands in π-cyclopentadienyl derivatives of transition metals. (*b*) Sequence of increasing shielding of ^{13}C and ^{1}H nuclei in π-cyclopentadienyl derivatives of transition metals.

this applies equally to the two β-atoms; but if an asymmetric atom is adjacent to the ring, spectral differences arise between α- and α'-, and between β- and β'-carbon-13 atoms. Here we are dealing with short-range and long-range intramolecular effects of asymmetric atoms.

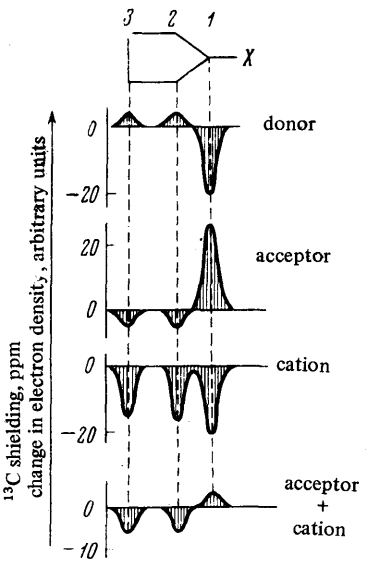


Figure 12. Variation in the shielding of carbon-13 nuclei in a cyclopentadienyl ligand of ferrocene under the influence of substituents attached to the α-carbon atom [107]. Donors (alkyls) increase the electron density at positions 2 and 3, but diminish it on the key atom. Acceptors (cyano and methine) decrease the electron density at positions 2 and 3, but increase it on the key carbon atom. A carbonium ion produces effects of the same sign, by diminishing electron density on all the atoms of cyclopentadiene ring. Substituents of mixed type (formyl, etc.), by producing competing effects of opposite sign at the key atom, cause a slight change in shielding of the key carbon-13 nucleus.

In the current physics of elementary particles fairly complicated views are held on the spatial, charge, and temporal symmetry of their interactions, on the relation between the charge and space parities of particles and antiparticles. As illustration, a neutrino is regarded as a kind of screw with a left-hand thread, and an antineutrino as one with a right-hand thread. Such properties are represented in scientific literature by terms such as "chirality" and "helicity", which imply "handedness" and "twistedness".

Study of the properties and interactions of optically active compounds with asymmetric atoms has revealed many curious new analogies between the chemistry and the physics of elementary particles, which have sometimes already been explained but occasionally still await a strict interpretation based on quantum mechanics and group theory. An example of such a new fact is the interesting phenomenon (Fig. 12) discovered by Kursanov et al. [108] that, when a cyclopentadienyl ring contains a substituent with a symmetrical atom directly adjacent to the ring, the two α-carbon-13 atoms have identical n.m.r. spectra, and

Many other examples of this kind have recently been investigated by Reutov et al. [109] for several classes of organoelementary compounds. A series of papers by Kabachnik and his coworkers [110,111] have demonstrated the effects of the intermolecular interaction of enantiomers, which has become possible only because of the exceptional absolute sensitivity of n.m.r. and the excellent reproducibility of the results. A definite chemical shift in the singlet phosphorus-31 n.m.r. spectrum is observed for a solution of "left-hand" molecules of biologically active phosphoric depsipeptides in an optically inactive solvent (chloroform); exactly the same shift is observed, of course, for a solution of "right-hand" molecules. With the same number of left- and right-hand molecules present an n.m.r. singlet is still observed, but displaced. In general, i.e. in a left–right mixture, two n.m.r. lines are present, whose positions and intensities depend on the relative concentrations of the two forms, as shown in Fig. 14. Thus "homocontacts" and "cross contacts" of left and right molecules in an inert solvent are different,

and their mutual shielding is non-equivalent. A pair of left and right molecules associate to form a diastereomer, which is short-lived on the n.m.r. time scale ($\tau \leqslant 10^{-3}$ s). It is of fundamental importance to investigate not only the analogy of, but also the possible effect of the asymmetry of elementary particles in our world on, the asymmetry at molecular and biological levels.

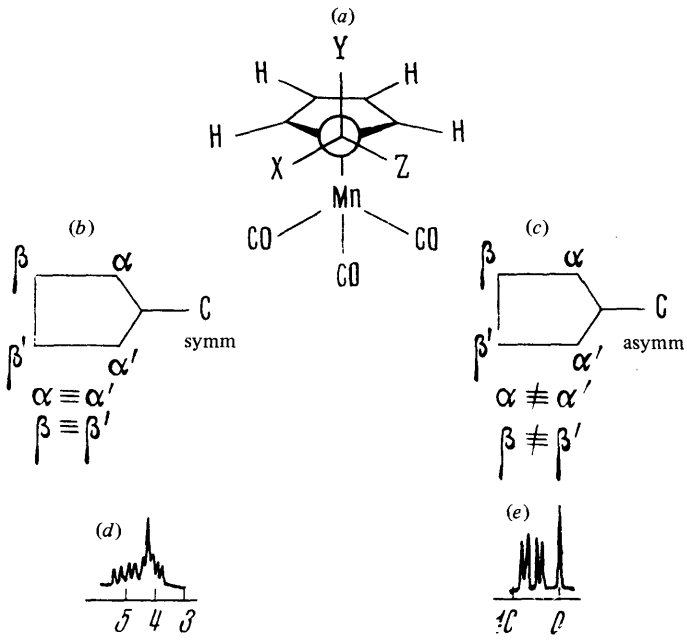


Figure 13. Increase in multiplicity of n.m.r. spectra of (*a*) cyclopentadienyltricarbonylmanganese under the influence of an asymmetric substituent[108,109]: (*b*) α- and β-carbon atoms chemically equivalent in pairs (giving a common n.m.r. signal) if the substituent is optically inactive; (*c*) all four carbon atoms in the substituted ring are chemically non-equivalent if the substituent is optically active; (*d*) ^{1}H n.m.r. spectrum; (*e*) ^{13}C n.m.r. spectrum.

Brief mention must be made of the extremely interesting work of Knunyants[112,113] on organofluorine compounds and of Andrianov[114-117] on organosilicon compounds. Comprehensive correlations between n.m.r. spectra and structure were obtained for both classes of compounds, and the chemical shifts of various fluorine-containing and silicon-containing functional groups were shown to be characteristic. Quantitative aspects of the effect of fluorine atoms on the carbon–mercury spin–spin interaction were obtained by Fourier carbon-13 n.m.r. spectroscopy. In molecules of the type R_2Hg, where R is a fluorine-containing substituent with sp^3 hybridisation of the α-carbon atom, only a small fraction of the observed spin interaction of the carbon-13 and mercury-199 nuclei is due to the usually prevalent Fermi contact mechanism.

A very peculiar reaction involving ring expansion in siloxanes has been discovered by means of n.m.r. spectroscopy. Furthermore, application of the method to organocyclosiloxanes led to a correct formulation of the converse problem, important for the method itself, which arises in interpreting the observed changes in chemical shifts and spin–spin interaction constants.

A clear and extremely important result at the level of the structure of complicated biomolecules has been obtained by Ovchinnikov et al.[118] working at the Shchemyakin Institute of Bio-organic Chemistry. Conformational rearrangements of the antibiotic valinomycin on complex formation with the potassium ion have been demonstrated by Fourier carbon-13 n.m.r. spectroscopy. Complex formation is accompanied by strong shifts (3–5.5 ppm) of the signals of the carbonyl groups to smaller magnetic fields, which is attributed both to the effect of hydrogen bonds and to the involvement of the carbonyl groups themselves in weak ion–dipole interaction retaining the potassium ion in the closed bud of valinomycin. Experiments finally confirmed a pattern of competition between intramolecular and intermolecular hydrogen bonds governing the bonding of ions in the central cavity of these beautiful, flowerlike cyclic molecules and their liberation on conformational opening of the bud, when the effect of the medium ruptures the intramolecular hydrogen bonds shown by double lines in Fig. 15*a*. These results are especially significant for the reason that the conformational rearrangements effect the transport of ions through cell membranes.

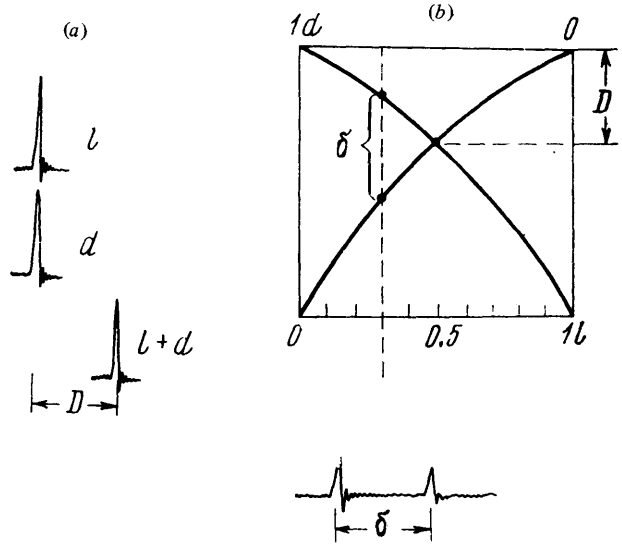


Figure 14. Statistically controlled diastereomeric association in solutions of enantiomers[110,111]: *a*) right-hand and left-hand molecules separately give a singlet n.m.r. signal with an identically coinciding chemical shift, which is displaced if they are mixed in equal quantities (deviation of chemical shift); *b*) with unequal concentrations of left-hand and right-hand molecules in solution the n.m.r. spectrum becomes a doublet, with the intensity ratio of the components equal to the concentration ratio.

Conditions of nuclear magnetic resonance are established by a strong and uniform external magnetic field, but in nuclear quadrupole resonance the three-dimensional quantisation of the magnetic moment of the nuclei is specified by intracrystalline electric field gradients which orient the nuclear quadrupole moments. The limited

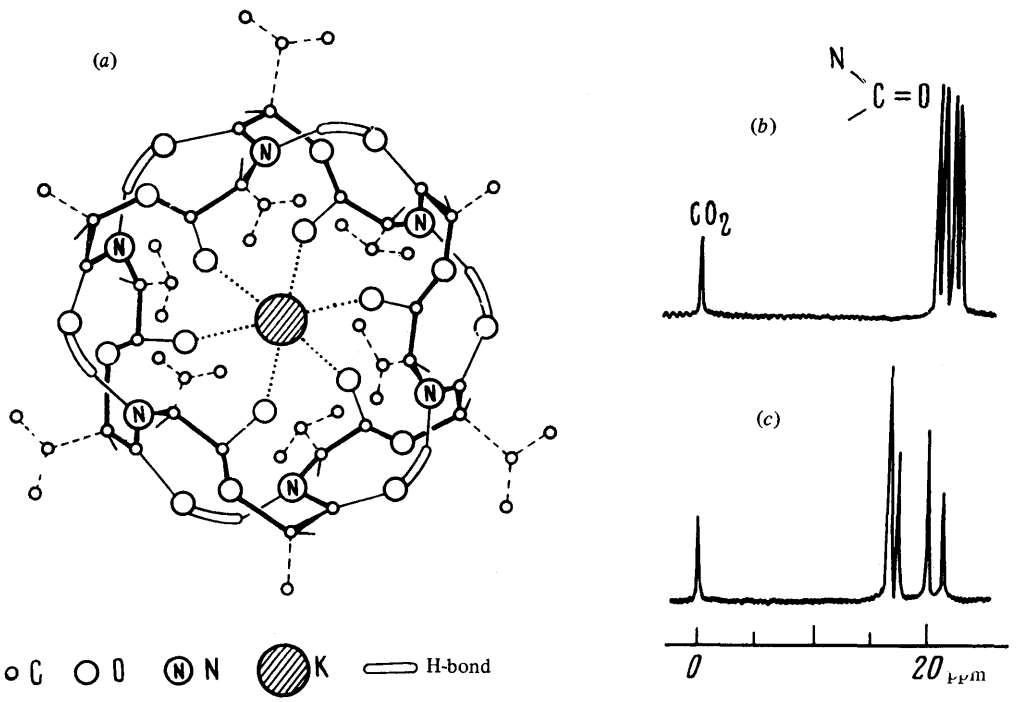


Figure 15. Observation of conformational rearrangement of valinomycin on complex formation with alkali-metal ions[118]: *a*) three-dimensional structure of potassium complex; *b*) position of n.m.r. signals of carbonyl groups in valinomycin; *c*) position in its potassium complex.

scope of the Review does not permit any detailed consideration of the work of Soviet scientists in applying nuclear quadrupole resonance to the study of the chemical structure of matter, although we have obtained the majority of the data on the chemical shifts of n.q.r. frequencies that have now accumulated in the world. Numerous correlations between n.q.r. frequencies and various σ-constants characterising the reactivity of molecules (such as the Hammett, Taft, etc. constants) have been established by the work of the Institute of Organoelementary Compounds[119,120], the Kazan chemical school of A.E. and B.A.Arbuzov[121], and also Voronkov[122]. Limitations have been revealed in the correlation approach, because several factors govern the relations between the electric field gradients on a given nucleus and the activity of the centres in different classes of reactions.

The applications of Mössbauer or γ-resonance spectroscopy to various fields of chemistry are universally associated primarily with the Institute of Chemical Physics. Investigations in this field were presented to the Annual General Meeting of the USSR Academy of Sciences in February 1966, and the lecture was subsequently published[122a], so that the present discussion will be confined to two or three significantly novel aspects. As early as 1962 the asymmetry of the γ-resonance spectra illustrated in Fig. 16 was discovered in the Institute. It permits detection and quantitative description of the anisotropy of bonds and vibrations of atoms in molecules and crystals from the type of spectra for isotropic polycrystalline powders, somewhat as the Debye method in X-ray diffraction gives the structure of single crystals from experiments on powders. During past years more than a hundred publications¶ have appeared on the above effect, which is referred in the world literature to Soviet scientists. A new effect of similar type was reported at the Institute in 1973, involving a difference between components of Mössbauer spectra not in peak area but in shape, whose study will permit characterisation of the anisotropic diffusion of molecular and supermolecular systems[133]. Use of emission γ-resonance spectroscopy, when the atoms are not in the stable form of absorbers but in the radioactive form of emitters of resonance γ-quanta, has opened up rich new possibilities for obtaining both structural and dynamic information.

Use of the iron-57 isotope as a Mössbauer label, with different spectra in all four forms—bivalent and tervalent, in high- and low-spin states—has shown convincingly[134] that the two classic coordination compounds familiar to all chemists since their student days of practical qualitative analysis—the beautiful Prussian Blue and Turnbull's Blue—are in fact the same compound (Prussian Blue), in which the high-spin outer-sphere ion is Fe^{3+}, while the low-spin inner-sphere iron is bivalent. However when these typical coordination compounds have been obtained, an electron escapes from the outer-sphere iron to the central ion of the complex, as illustrated by Fig. 17.

The first experiments by emission γ-resonance spectroscopy, when radioactive cobalt-57 was used as label

¶ Several interesting publications of recent years may be mentioned as example[123-132].

and the chemical state of iron-57 atoms formed by K-capture in the cobalt isotope was determined, supported the above conclusions. Subsequently, however, use was made of the fact that emission of a resonance γ-quantum of energy 14 keV by an excited iron-57 nucleus is preceded by the escape of another, harder quantum (123 keV–Fig. 18), and the time dependence of the form of the Mössbauer spectra of the hexacyanoferrate(II–III) complexes was studied. In this way it was possible to characterise an extremely unstable form of Turnbull's Blue at the instant of its formation[135], and to establish that the time of intramolecular electron transfer converting the complex into Prussian Blue was close to 10^{-8} s.

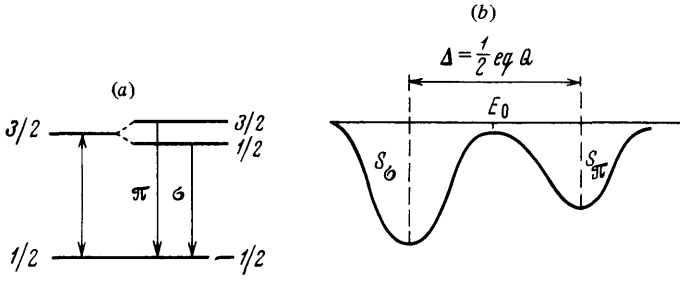


Figure 16. Illustration of effect of asymmetry of hyperfine structure of γ-resonance spectra due to anisotropy of motion of Mössbauer atoms: *a*) scheme of $\frac{3}{2} \rightarrow \frac{1}{2}$ transition in the quadrupole splitting of upper level (π-transition $\frac{3}{2} \rightarrow \frac{1}{2}$; σ-transition $\frac{1}{2} \rightarrow \frac{1}{2}$); *b*) asymmetry of Mössbauer quadrupole doublet for isotropic powdered specimen with different mean square amplitudes of vibration $\overline{x^2}$ and $\overline{z^2}$ perpendicular and parallel to the direction of the gradient q of the electric field in a molecule or in a crystal (s_σ and s_π are the areas of the peaks).

As a method sensitive both to the electronic structure and to the motion of atoms and electrons, γ-resonance spectroscopy should undoubtedly in future occupy a prominent position in molecular biology for the study of numerous examples of the interrelation between the transport of electrons and changes in electronic states with particular mechanical movements. A most important problem in molecular biology is the mechanism of photoreception—the nature of the action of light on visual pigments and photoreceptor membranes—with which the "rhodopsin" project headed by Yu. A. Ovchinnikov is concerned. An extremely interesting result has recently been obtained in the Institute of Chemical Physics by collaboration between the Structure of Matter Department and N. M. Emanuel's department[136]. This was based entirely on the unique possibilities of simultaneously revealing both the electronstructural and the dynamic properties of a substance by means of γ-resonance spectroscopy. It has been established that the first stage of photolysis of the pigment—conversion of rhodopsin into prelumirhodopsin—is already accompanied not only by photoisomerisation of the chromophore (11-*cis*-retinal → 11-*trans*-retinal) but also by reversible conformational rearrangement of the whole photoreceptor membrane, which occurs even at extremely low temperatures (77°K) and leads to a sharp increase in the rate of spin–lattice relaxation.

The relative accuracy of γ-resonance spectroscopic measurements has no equal: fractional energy changes of the spectral lines of 10^{-15}–10^{-16} have already been recorded; this improves the relative accuracy of nuclear magnetic resonance by factors of 10^5–10^6. However, the energies of the transitions between two nuclear levels

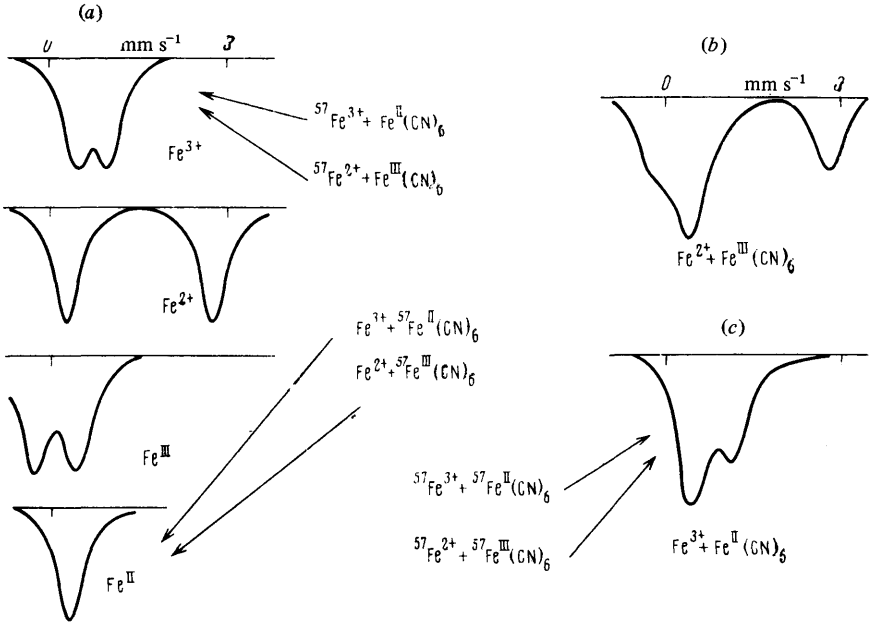


Figure 17. γ-Resonance spectra of hexacyanoferrate(II–III) complexes (only the spectra indicated by the arrows are observed): *a*) high-spin and low-spin forms of bivalent and tervalent iron; *b*) Fe^{2+} + Fe^{III} (Turnbull's Blue); *c*) Fe^{3+} + Fe^{II} (Prussian Blue).

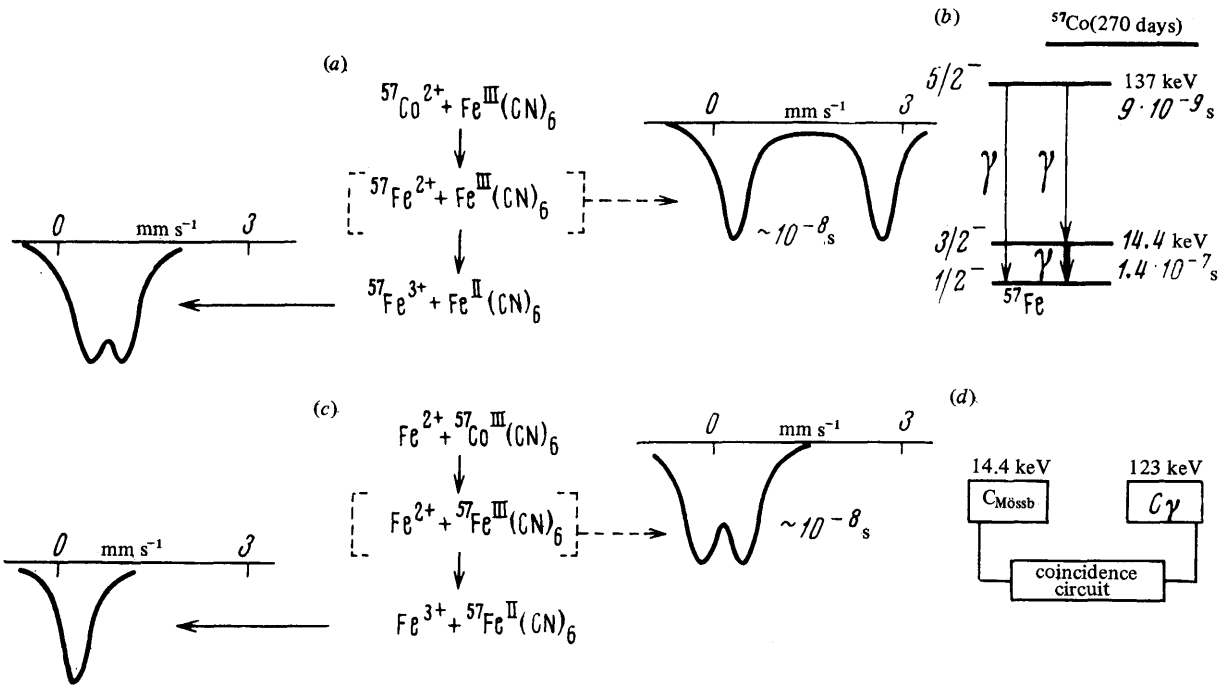


Figure 18. γ-Resonance emission spectra of systems formed by K-capture by cobalt-57 nuclei of: *a*) outer-sphere Co^{2+} with a hexacyanoferrate(III) anion—spectra integrated with time ($> 10^{-7}$ s) after the disintegration $^{57}Co \rightarrow {}^{57}Fe$); *b*) spectra of system (*a*) ~ 10^{-8} s after the disintegration; *c*) hexacyanocobaltate(III) anion with outer-sphere Fe^{2+} cation—spectra integrated with time ($> 10^{-7}$ s) after the disintegration; *d*) spectra of system (*c*) ~ 10^{-8} s after the disintegration.

used in the Mössbauer effect are reckoned in tens of electron-kilovolts, exceeding by almost a billion (10^{12}) the typical energies of n.m.r. transitions. Because of the scatter of local electric and magnetic fields and the presence of all kinds of defects, dislocations, etc., furthermore, the strongest non-uniform broadening of the spectral lines occurs when two different nuclei—an emitter and an absorber of γ-quanta—are involved in the resonance transition. Hitherto, therefore, it has not been possible to observe in Mössbauer spectra absolute line widths below 10^{-10} eV, which is wider than the best n.m.r. lines by a factor of 10^7. This fact played a decisive part in the unsuccessful plans of all kinds to produce a γ-ray laser, abandoned over a decade ago. During the past two or three years, however, fundamentally new ideas have appeared in papers by Soviet scientists—Kagan, Khokhlov, the present Reviewer, and others[137,138]—opening the way to produce γ-ray lasers both on lines of great natural width (i.e. on short-lived nuclei) with neutron pumping and by eliminating various forms of line broadening by combining the methods of γ-ray resonance spectroscopy and nuclear magnetic resonance. Furthermore, an original laser method has been suggested for separating nuclei excited to the Mössbauer levels necessary for stimulating γ-emission from the same nuclei in the ground state[139]. Work aimed at producing a γ-ray laser is of very great interest to physics, chemistry, and biology, for powerful beams of coherent radiation are apparently able to produce direct holographic three-dimensional images of molecules.

We have been considering above the use of hyperfine interactions between electrons and nuclei to study the structure of matter. Considerable successes have also attended quantitative observations of the interaction between electrons of outer and inner shells. The well known phenomenon of the photoeffect—the dislodgment of an inner or a valency electron by a quantum of definite energy—underlies X-ray electron or photoelectron spectroscopy, and the kinetic energy of the electron is measured in the most accurate β-spectrometer. The binding energy of an electron in chemically combined atoms is determined from the difference between the energy of the quantum and the kinetic energy. This quantity is a sensitive characteristic of the chemical bond: with its help we can use data on relative line intensities to construct diagrams of valency and inner electron levels, to determine the degree of oxidation of an element and the donor–acceptor character of a ligand in a complex, to solve many problems of the geometrical structure of a molecule, to estimate the effective charge on an atom, to make a quantitative analysis of elements and functional groups, and to study adsorbed molecules, catalysts, diffusion, the composition of the thinnest surface films, etc. Broad investigations in this field were begun in the Kurnakov Institute of General and Inorganic Chemistry at the end of 1970, and more than 500 simple

and complex inorganic compounds have been examined during the past three years. Some of the most interesting and important results[140] will be noted here.

Examination of specimens of a lunar regolith provided by Soviet automatic stations and by American cosmonauts has shown that the concentrations of elements at the surface of the particles differ appreciably and regularly from the bulk concentrations. A substantial part of the surface consists of metallic iron, coated with only an unusually thin layer of oxide or even in part not oxidised at all after a long time in the earth's atmosphere (Vinogradov, Zhavoronkov et al.[141,142]).

Study of a large number of isostructural series of complex compounds of platinum, palladium, rhodium, iridium, cobalt, and other transition metals has established sequences of ligands according to their ability to withdraw electron density from the central atom[140]. The sequence for acido-ligands is

$$F > NO_3 \gtrsim NO_2 \gtrsim CN \simeq \tfrac{1}{2}C_2O_4 \simeq NCS > Cl > Br \simeq SCN > I$$

the corresponding sequence for neutral ligands is

$$N_2 > CO \simeq C_2H_4 > C_2(C_6H_5)_2 > C_6H_5CN > NH_3 > C_5H_5N > R_2S > P(C_6H_5)_3$$

Buslaev et al.[143] have obtained schemes of molecular valency levels for oxo-anions and fluorides of non-transition elements in Groups II–V, and have established for the first time several regularities in the variation of energy levels of isoelectronic and isovalent series of compounds. These rules are supported by calculations[144]. Detailed consideration has been given to experimental and theoretical aspects of the determination of relative line intensities in an X-ray electron spectrum. A technique developed for the quantitative analysis of thin films on solid surfaces has been used to examine the surface characteristics of catalysts, semiconductors, certain protective coatings, etc.

Although electron spectroscopy for chemical analysis in its X-ray form (X-ray electron spectroscopy) has reached us from abroad, accurate chemical X-ray spectroscopy owes not only its fruitful application but also its actual origin to Soviet scientists. Chemical changes in the energy of X-ray lines, like the ionisation potentials of the inner electrons, are governed by the shielding effect of the outer electron shells on the inner shells. It was established as early as the 1920s that the energies of X-ray transitions are slightly dependent on the chemical bond, but only in the 1960s were methods first proposed, as a consequence of development of the appropriate quantum-chemical techniques in the Institutes of the USSR Academy of Sciences[77-83,145], for determining the effective atomic charges in molecules from the shifts in the lines of the X-ray emission spectrum. These methods are based on the principle that the magnitude of the shift is completely determined by the number and the character of the valency electrons belonging to the given atom. The effective charge on an atom in a compound is found from this relation and the measured shift of the X-ray line. At the present time the X-ray spectroscopic method for determining the effective charge on an atom is probably the most soundly based, and is widely used in Soviet and foreign laboratories. Measurement of the shift of the inner X-ray lines provides solutions in particular to the problems of the degree of oxidation of an element in a compound, the presence of non-equivalent atoms of the same element in a compound, and the coordination numbers of certain elements, and permits the study of several other characteristics of the geometrical structure of molecules.

Extremely important information on the electronic structure of chemical compounds (the ionisation energies of valency levels and the character of their wave functions) can be extracted from the energies and the relative intensities of X-ray transitions from valency levels and bands. For example, the relative intensities of the maxima in the K-spectrum of chlorine can be used to determine the ratio of the squares of the coefficients in the $3p$ orbitals of the chlorine atom in all the wave functions of the valency levels, and the energy position of the maxima to find the relative positions of the valency levels. Since the X-ray spectra of almost all the atoms in a compound can be studied, a fairly detailed picture of the electronic structure of the molecule is obtained. Work on the chemical X-ray spectroscopy of free molecules and isolated groups in crystals, semiconductors, and metals has been done in several Institutes of the USSR Academy of Sciences—the Kurnakov Institute of General and Inorganic Chemistry[146], the Institute of Inorganic Chemistry of the Siberian Division (Nikolaev et al.[147]), and the Institute of Metal Physics of the Ural Science Centre[148]—the Institute of Metal Physics of the Ukrainian SSR Academy of Sciences[149], etc.

The chemical bond has been investigated also by use of the fine structure of the edges of X-ray absorption spectra, which corresponds to electron transitions from inner levels to vacant levels of the discrete and continuous spectrum. These transitions can be used to construct a scheme of vacant levels and to determine the effective charge on the absorbing atom. The first method for such determination was developed in the Vernadskii Institute of Geochemistry and Analytical Chemistry and the Institute of the Mineralogy, Geochemistry, and Crystal Chemistry of the Rare Elements of the USSR Academy of Sciences[77-80], and was based on the dependence of the energy position of the discrete absorption lines and their relative intensity on the effective charge of the absorbing atom. This method stimulated the study of X-ray absorption spectra, and on its basis the problem of the relative intensities of the discrete spectrum and the origin of the continuous absorption spectrum was first posed and solved for the simplest model. Until the mid-1960s accurate chemical X-ray spectroscopy was confined to elements at the beginning and the middle of the periodic system. X-Ray methods for determining effective charges on atoms even of the heaviest elements were subsequently developed from work at the Konstantinov Leningrad Institute of Nuclear Physics of the USSR Academy of Sciences[81-83]. This new type of spectroscopy thereby acquired universal value.

Chemical X-ray spectroscopy provided a very clear demonstration of the particular inadequacy of formal ideas on the oxidation states of atoms. The determination of effective charges from X-ray emission and absorption spectra sometimes led to quite remarkable conclusions[77,78]. For example, whereas the effective charges in high-spin compounds of bivalent iron were only slightly less than the formal valency of the ion (2+), in the analogous compounds of tervalent iron these charges were not simply very far from the formal valency of the ion (3+) but, moreover, even smaller than for bivalent iron, about +1.2. The effective charges on iron in ferrocene and the ferricinium ion (where one electron has been removed) were almost identical (about +0.6). The effective charges of cations are in general always less than their formal valencies, while the charges on anions are numerically less than unity: in other words, Coulombic repulsion prevents the accommodation of more than one extra electron in an atom, after which only a redistribution of electrons

among different molecular orbitals takes place. In just the same way a large positive charge on an ion is balanced by electrons (which "leak" from other parts of the molecule) from other molecular orbitals. Therefore, as in the ferricinium ion it is not the central iron atom but the cyclopentadienyl ring which is ionised; in the ion $[Fe(H_2O)_6]^{3+}$, however, ligands (water molecules)—not the iron itself—lose three electrons. Although the calculation of effective atomic charges in molecules and the significance attributable to these quantities, in particular the volume in which the measured charge is concentrated, continue to be debated†, the positive side of the conclusions is undoubted: the electrostatic description of chemical bonds is decisively rejected even in high-spin compounds having a weak ligand field (which were the most reliable "refuge" of electrostatic concepts); the rightness and also in some measure validity of such an empirical generalisation as Pauling's principle of electrical neutrality are confirmed; and finally the need to apply the currently most popular and fruitful method of quantum chemistry—molecular orbital theory—to almost all chemical structures is convincingly demonstrated.

Modern structural chemistry makes use of radiation covering a range of more than thirty octaves (10^{10} of wavelengths, from fractions of an Ångström unit to decimetres). Different methods give, of course, complementary information, and only the combination of all methods will yield a consistent picture of the electronic structure of atoms and molecules. Owing to the impossibility of obtaining exact solutions to the Schrödinger equation for many-electron systems, chemists are compelled to use only approximate solutions. As a consequence, even in the most favourable case the complete wave function of a many-electron system—atom or molecule—can be sufficiently accurate only in certain of its regions: in other words, a wave function which may be entirely adequate e.g. for analysing the electronic spectrum of a molecule may prove completely unsuitable for describing the n.m.r., e.s.r., or γ-resonance spectrum of the same molecule.

The development of numerous spectroscopic methods enabling the various parts of many-electron systems to be "probed" has seriously tested theoretical methods of obtaining the wave functions of atoms and molecules. During the past decade this has greatly disturbed the coexistence of different approximate theories of the chemical bond, and one of them—the theory of molecular orbitals—has clearly tended to be preferred by research workers. This theory is based on the formation in a molecule of discrete states of individual electrons (molecular orbitals), defined by the self-consistent motion of the electrons in the field produced by the others and all the nuclei in the molecule. Thus the quantum-mechanical model of an atom—the theory of atomic orbitals—now represents the particular case in molecular-orbital theory in which the system contains only one atomic nucleus. Furthermore, the molecular-orbital theory involves the most general physical concepts on molecular structure, and the mathematics used is most suitable for making quantitative calculations on an electronic computer. All this is responsible for the dominant role of this theory in modern quantum chemistry.

One of the first to make wide use of the molecular orbital method and to popularise it in every way possible was Ya. K. Syrkin[150-152], founder of the Soviet school of quantum chemistry. He clearly demonstrated with numerous examples (including the effective charges on atoms in molecules[151]) the need to regard the properties of a molecule not as the simple sum of those of central ion and ligands but as involving all the intramolecular interactions, by no means reducible to small perturbations. Soviet scientists were the first to make systematic calculations by a form of the method which has since found widespread use in the so called zero differential overlap approximation (ZDO)[152,153], also to use the method to describe transition-metal complexes, including sandwich compounds[154,155], and to analyse the band structure of dielectrics and semiconductors[156].

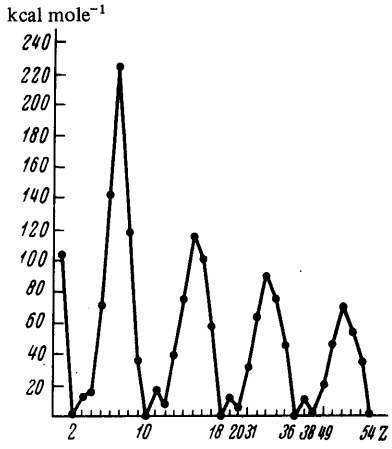


Figure 19. Stabilities (dissociation energies) of homonuclear diatomic molecules Z_2 for elements in the main groups of the first five periods of Mendeleev's system.

In conclusion let us consider briefly the periodicity of the chemical properties of the elements in the light of our modern knowledge of molecules. The molecular-orbital theory, which extends and generalises the atomic-orbital theory, regards the electronic structure of a molecule as resulting from the filling of discrete electron levels forming definitely repeated shells by virtue of the laws of quantum mechanics and the Pauli principle. Thus, just as periodic relations exist in the electronic structure of atoms, so also distinct periodic variations (though more complicated) are found in the electronic structure of molecules. A convincing example is the clear correlation of various properties of homonuclear diatomic molecules (e.g. the stability, i.e. the dissociation energy, of Z_2 in Fig. 19) with the position of the atom Z in the periodic system[157]. Here the sequence of molecular orbitals, bonding and antibonding in character, is almost invariant in Z_2 molecules for all atoms of a given period. The differing properties of these molecules depend on the relative numbers of bonding and antibonding electrons, which is ultimately determined by the total number of electrons

† The concept of the effective charges of atoms is most justified when such charges are compared in series of compounds of the same type, e.g. monosubstituted compounds or complexes of a given element with ligands having weak and strong fields respectively.

in the molecule, i.e. by the atomic number of the element Z. This is yet another of the innumerable confirmations expected by Mendeleev in the future superstructure and development of the periodic law.

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We have tried to trace the main line of research on the structure of matter from the establishment of Mendeleev's periodic law until the present time. These investigations provide the clearest evidence of the unity and indissolubility of the whole of modern natural science—primarily physics, chemistry, and biology—most closely linked with ideas on the structure of matter, from elementary particles to the most complicated molecules and cells. Indeed, the properties of elementary particles that have now been found and explained on the Mendeleev path of the development of physics and chemistry, interactions between nuclei and electron shells, have become the basis of methods correctly revealing the structure of molecules and the relation between this structure and their reactivity, i.e. the spatial rearrangement and movement of molecules, which means solving key problems both of theoretical chemistry and of future chemical industry, as well as understanding the molecular nature of the motion of biological materials. Contrary to the view sometimes held, the role of chemistry in this triad (physics, chemistry, biology) has by no means become subordinate, but is even central, for without chemistry a genuine union and mutual enrichment of the main natural sciences are impossible.

BIBLIOGRAPHY‡

1. "Arkhiv D. I. Mendeleeva" (Archives of D. I. Mendeleev), Moscow, 1951, Vol. 1, p. 34.
2. D. I. Mendeleev, "Izbrannye Sochineniya" (Selected Works), Moscow, 1934, Vol. 2, p. 111.
3. I. V. Kourtchatov, B. V. Kourtchatov, L. V. Misowski, and L. I. Roussinov, Compt. rend., **200**, 1201 (1935).
4. K. A. Petrzhak and G. N. Flerov, Zhur. Eksper. Teor. Fiz., **10**, 1013 (1940).
5. B. S. Dzhelepov, Izv. Akad. Nauk, Ser. Fiz., **15**, 496 (1951).
6. V. I. Gol'danskii, Zhur. Eksper. Teor. Fiz., **39**, 497 (1960); Nuclear Phys., **19**, 482 (1960); Uspekhi Fiz. Nauk, **87**, 255 (1965).
7. V. A. Karnaukhov and N. I. Tarantin, Zhur. Eksper. Teor. Fiz., **39**, 1107 (1960).
8. J. Cerny, J. E. Esterl, R. A. Gough, and R. G. Sextro, Phys. Letters, **33**, (B), 284 (1970).
9. V. I. Gol'danskii and L. K. Peker, Pis'ma Zhur. Eksper. Teor. Fiz., **13**, 577 (1971).
10. V. A. Karnaukhov, G. M. Ter-Akop'yan, and V. G. Subbotin, Preprint OIYaI (JINR Comm.) R. 1072, Dubna, 1962.
11. V. I. Kuznetsov, N. K. Skobelev, and G. N. Flerov, Yadernaya Fiz., **4**, 279 (1966); **5**, 271 (1967); **15**, 444 (1972).
12. E. E. Berlovich and Yu. N. Novikov, Izv. Akad. Nauk SSSR, Ser. Fiz., **33**, 679 (1966); Dokl. Akad. Nauk SSSR, **185**, 1025 (1969).
13. Ya. V. Zel'dovich, Zhur. Eksper. Teor. Fiz., **38**, 1123 (1960).
14. A. I. Baz', V. I. Gol'danskii, and Ya. B. Zel'dovich, Uspekhi Fiz. Nauk, **72**, 211 (1960); **85**, 445 (1965).
15. Yu. N. Batusov, S. A. Bunyatov, V. I. Gol'danskii, Ya. B. Zel'dovich, O. V. Lozhkin, A. A. Rimskii-Korsakov, V. M. Sidorov, and V. A. Yarba, "Otkrytie" (Discovery) No. 119; Otkrytiya, Izobreteniya, Promyshlennye Obraztsy i Tovarnye Znaki, No. 36, 1 (1972).
16. G. I. Seaborg, "Man-made Transuranium Elements" (Translated into Russian), Inostr. Lit., Moscow, 1965, p. 49.
17. G. T. Seaborg, in "Sbornik Sto Let Periodicheskogo Zakona Khimicheskikh Elementov" (One Hundred Years of the Periodic Law of the Chemical Elements), Nauka, Moscow, 1969, p. 136.
18. G. T. Seaborg, "Vtoroi Sbornik Sto Let Periodicheskogo Zakona Khimicheskikh Elementov" (Second Volume—"One Hundred Years of the Periodic Law of the Chemical Elements"), Nauka, Moscow, 1971, p. 21.
19. G. T. Seaborg, J. L. Crandall, P. R. Fields, A. Ghiorso, O. L. Keller, and R. A. Penneman, in "Uchenie o Radioaktivnosti" (The Science of Radioactivity), Nauka, Moscow, 1973, p. 183.
20. G. N. Flerov and I. Zvara, see Ref. 17, p. 115.
21. G. N. Flerov, see Ref. 18, p. 11.
22. G. N. Flerov, see Ref. 19, p. 172.
23. G. N. Flerov and I. Zvara, "Khimicheskie Elementy Vtoroi Sotni" (The Second Hundred Chemical Elements), Preprint OIYaI (JINR Comm.) D7-6013, Dubna, 1971.
24. G. N. Flerov, Yu. Ts. Oganesyan, Yu. V. Lobanov, V. I. Kuznetsov, V. A. Druin, V. P. Perelygin, K. A. Gavrilov, S. P. Tret'yakova, and V. M. Plotko, Atomnaya Energiya, **17**, 310 (1964).
25. G. N. Flerov, Yu. Ts. Oganesyan, Yu. V. Lobanov, Yu. A. Lazarev, and S. P. Tret'yakova, Atomnaya Energiya, **29**, 243 (1970).

25a. Laboratory of Nuclear Reactions, OIYaI Preprint (JINR Comm.) D7-8099.

26. N. N. Krot and A. D. Gel'man, Dokl. Akad. Nauk SSSR, **177**, 124 (1967).
27. V. I. Spitsyn, N. N. Krot, M. P. Mefod'eva, and A. D. Gel'man, Dokl. Akad. Nauk SSSR, **181**, 128 (1968).
28. V. I. Spitsyn, see Ref. 17, p. 225.
29. A. D. Gel'man, N. N. Krot, and M. P. Mefod'eva, "Otkrytie" (Discovery) No. 96; Otkrytiya, Izobreteniya, Promyshlennye Obraztsy i Tovarnye Znaki, No. 25, 1 (1971).
30. N. N. Krot, V. P. Shilov, V. B. Nikolaevskii, A. K. Pikaev, A. D. Gel'man, and V. I. Spitsyn, Dokl. Akad. Nauk SSSR, **217**, 589 (1974).
31. N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, N. A. Rozenkevich, I. A. Rumer, and L. N. Auerman, Radiokhimiya, **14**, 486 (1972).
32. N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, B. A. Gvozdev, V. A. Druin, I. A. Rumer, R. A. D'yachkova, N. A. Rozenkevich, and L. N. Auerman, Dokl. Akad. Nauk SSSR, **201**, 1393 (1971).
33. N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, I. A. Rumer, B. A. Gvozdev, N. A. Rozenkevich, and L. N. Auerman, Dokl. Akad. Nauk SSSR, **208**, 1146 (1973).
34. I. Zvara, Yu. T. Chuburkov, R. Caletka, T. S. Zvarova, M. R. Shalaevskii, and B. V. Shilov, Atomnaya Energiya, **21**, 83 (1966).

‡ This list of references makes no claim to be complete and serves only for illustrative purposes. When too many references are available on a particular problem, preference is given to review papers or the earliest and latest publications.

35. I. Zvara, Yu. T. Chuburkov, V. Z. Belov, G. V. Buklanov, B. B. Zakhvataev, T. S. Zvarova, O. D. Maslov, R. Caletka, and M. R. Shalaevskii, J. Inorg. Nuclear Chem., **32**, 1885 (1970).
36. I. Zvara, V. Z. Belov, Yu. S. Korotkin, M. R. Shalaevskii, V. A. Shchegolev, M. Hussonois, and B. A. Zager, JINR Comm. R12-5120, Dubna, 1970.
37. I. Zvara, JINR Comm. E12-7547, Dubna, 1973.
38. W. D. Myers and W. J. Swiatecki, Nuclear Phys., **81**, 1 (1966).
39. V. M. Strutinskii and Yu. A. Muzychka, "Trudy Mezhdunarodnoi Konferentsii po Fizike Tyazhelykh Ionov" (Proceedings of an International Conference on the Physics of Heavy Ions), Dubna, 1966, Vol. 2, p. 51.
40. J. Grumann, U. Mosel, B. Fink, and W. Greiner, Z. Physik, **228**, 371 (1969).
41. V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, **180**, 1360 (1968).
42. G. T. Seaborg, see Ref. 17, p. 136.
43. V. I. Gol'danskii and V. G. Firsov, Uspekhi Khim., **40**, 1353 (1971) [Russ. Chem. Rev., No. 8 (1971)].
44. V. I. Gol'danskii, "Fizicheskaya Khimiya Pozitrona i Pozitroniya" (Physical Chemistry of the Positron and of Positronium), Nauka, Moscow, 1968.
45. V. I. Gol'danskii and V. P. Shantarovich, "Proceedings of the Second International Conference on the Annihilation of Positrons, Kingston, Canada, 1971", pp. 5–1; Appl. Phys., 3, 111 (1974).
46. V. G. Firsov and V. M. Bakov, Zhur. Eksper. Teor. Fiz., **47**, 1074 (1964).
47. V. G. Firsov, Zhur. Eksper. Teor. Fiz., **48**, 1179 (1965).
48. G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, and V. G. Firsov, Khim. Vysok. Energii, **1**, 387 (1967).
49. G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, and V. G. Firsov, Khim. Vysok. Energii, **3**, 510 (1969).
50. G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, and V. G. Firsov, Khim. Vysok. Energii, **4**, 447 (1970).
51. V. G. Nosov and I. V. Yakovleva, Zhur. Eksper. Teor. Fiz., **43**, 1750 (1962).
52. I. G. Ivanter and V. P. Smilga, Zhur. Eksper. Teor. Fiz., **55**, 1521 (1968).
53. I. G. Ivanter, E. V. Minaichev, G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, G. I. Savel'ev, V. P. Smilga, and V. G. Firsov, Zhur. Eksper. Teor. Fiz., **62**, 14 (1972).
54. I. G. Ivanter, E. A. Meleshko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, V. P. Smilga, B. V. Sokolov, and V. D. Shestakov, Zhur. Eksper. Teor. Fiz., **60**, 471 (1971).
55. I. I. Gurevich, L. A. Makar'ina, E. A. Meleshko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, and B. V. Sokolov, Zhur. Eksper. Teor. Fiz., **54**, 432 (1968).
56. I. I. Gurevich, A. I. Klimov, V. N. Maiorov, S. A. Meleshko, I. A. Muratov, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, and V. A. Suetin, Zhur. Eksper. Teor. Fiz., **66**, 374 (1974).
57. V. G. Zinov, A. D. Konin, and A. I. Mukhin, Yadernaya Fiz., **2**, 859 (1965).
58. A. F. Dunaitsev, V. I. Petrukhin, Yu. D. Prokoshkin, and V. I. Rykalin, Zhur. Eksper. Teor. Fiz., **42**, 1680 (1962).
59. V. I. Petrukhin and Yu. D. Prokoshkin, Dokl. Akad. Nauk SSSR, **160**, 71 (1965).
60. L. I. Ponomarev, Yadernaya Fiz., **2**, 223 (1965).
61. S. S. Gershtein, V. I. Petrukhin, L. I. Ponomarev, and Yu. D. Prokoshkin, Uspekhi Fiz. Nauk, **97**, 3 (1969).
62. L. I. Ponomarev, Ann. Rev. Nuclear Sci., **23**, 395 (1973).
63. V. I. Gol'danskii, A. A. Dzhuraev, V. S. Evseev, Yu. V. Obukhov, V. S. Roganov, M. V. Frontas'eva, and N. I. Kholodov, Dokl. Akad. Nauk SSSR, **211**, 316 (1973).
64. V. I. Gol'danskii, N. N. Zatsepina, V. I. Petrukhin, V. E. Risin, V. M. Suvorov, I. F. Tupitsyn, N. I. Kholodov, and I. A. Yutlandov, Dokl. Akad. Nauk SSSR, **214**, 1105, 1337 (1974).
65. V. S. Evseev, Preprint OIYaI (JINR Comm.) R 14-4052, Dubna, 1968.
66. A. A. Dzhuraev and V. S. Evseev, Zhur. Eksper. Teor. Fiz., **62**, 1166 (1972).
67. A. A. Dzhuraev, V. S. Evseev, Yu. V. Obukhov, and V. S. Roganov, Zhur. Eksper. Teor. Fiz., **66**, 433 (1974).
68. L. N. Dobrezov and A. N. Terenin, Naturwiss., **16**, 656 (1928).
69. H. Schüler, Naturwiss., **16**, 512 (1928).
70. E. K. Zavoiskii, Doctoral Thesis, Lebedev FIAN, Moscow, 1944.
71. E. K. Zavoiskii, J. Phys. USSR, **9**, 211, 245 (1945).
72. V. I. Gol'danskii, "Effekt Mëssbauera i ego Primeneniya v Khimii" (The Mössbauer Effect and its Application in Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1963.
73. "Chemical Applications of Mössbauer Spectroscopy", V. I. Gol'danskii and R. H. Herber (Editors), Academic Press, New York, 1968.
74. C. Nordling, E. Sokolowski, and K. Siegbahn, Phys. Rev., **105**, 1676 (1957).
75. K. Siegbahn, C. Nordling, A. Falman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "Electron Spectroscopy for Chemical Analysis" (Translated into Russian), Mir, Moscow, 1971.
76. V. L. Kurbatov, F. I. Vilesov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, **138**, 1329 (1961); **141**, 1343 (1961).
77. E. E. Vainshtein, R. L. Barinskii, and K. I. Narbutt, Zhur. Eksper. Teor. Fiz., **23**, 593 (1952).
78. R. L. Barinskii, E. E. Vainshtein, and K. I. Narbutt, Izv. Akad. Nauk SSSR, Ser. Fiz., **21**, 1351 (1957).
79. V. I. Nefedov, Zhur. Strukt. Khim., **5**, 651 (1964).
80. R. L. Barinskii and V. I. Nefedov, "Rentgenospektral'noe Opredelenie Zaryada Atomov v Molekulakh" (X-Ray Spectroscopic Determination of Charges on Atoms in Molecules), Nauka, Moscow, 1966.
81. O. I. Sumbaev and A. F. Mezentsev, Zhur. Eksper. Teor. Fiz., **48**, 445 (1965).
82. O. I. Sumbaev, Zhur. Eksper. Teor. Fiz., **57**, 1716 (1969).
83. E. V. Petrovich, Yu. P. Smirnov, V. S. Zykov, A. I. Grushko, O. I. Sumbaev, I. M. Band, and M. B. Trokanovskaya, Zhur. Eksper. Teor. Fiz., **61**, 1756 (1971).
84. R. V. Ambartsumyan, V. S. Letokhov, G. I. Makarov, and P. A. Puretskii, Dokl. Akad. Nauk SSSR, **211**, 365 (1973).
85. S. A. Al'tshuler, B. M. Kozyrev, and S. G. Salikhov, Dokl. Akad. Nauk SSSR, **71**, 855 (1950).
86. R. P. Penrose, Nature, **163**, 992 (1949).

87. L. A. Blyumenfel'd, V. V. Voevodskii, and A. G. Semenov, "Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii" (Application of Electron Spin Resonance in Chemistry), Izd. Sibirsk. Otd. Akad. Nauk SSSR, Novosibirsk, 1962.
88. V. V. Voevodskii and L. A. Blyumenfel'd, Zhur. Vses. Khim. Obshch. Mendeleeva, 7, 457 (1962).
89. L. A. Blyumenfel'd, V. I. Gol'danskii, M. I. Podgoretskii, and D. S. Chernavskii, Zhur. Strukt. Khim., 8, 854 (1967).
90. V. V. Voevodskii, S. P. Solodovnikov, and V. M. Chibrikin, Dokl. Akad. Nauk SSSR, 129, 1082 (1959).
91. A. B. Shapiro, M. G. Goldfield, and E. G. Rozantzev, Tetrahedron Letters, 2183 (1973).
92. V. I. Gol'danskii, K. I. Zamaraev, A. I. Mikhailov, and R. F. Khairutdinov, in "Problemy Kinetiki Elementarnykh Khimicheskikh Reaktsii" (Problems of the Kinetics of Elementary Chemical Reactions), Nauka, Moscow, 1973, p. 68.
93. A. I. Mikhailov, A. I. Bol'shakov, Ya. S. Lebedev, and V. I. Gol'danskii, Fiz. Tverd. Tela, 14, 1172 (1972).
94. V. N. Panfilov, Yu. D. Tsvetkov, and V. V. Voevodskii, Kinetika i Kataliz, 1, 333 (1960).
95. V. N. Panfilov, in "Svobodno-radikal'nye Sostoyaniya v Khimii" (Free-radical States in Chemistry), Izd. Sibirsk. Otd. Akad. Nauk SSSR, Novosibirsk, 1972.
96. A. B. Nalbandyan, Uspekhi Khim., 35, 587 (1966) [Russ. Chem. Rev., No. 4 (1966)].
97. T. A. Garibyan, G. L. Grigoryan, A. A. Mantashyan, and A. B. Nalbandyan, Dokl. Akad. Nauk SSSR, 177, 149 (1967).
98. A. B. Nalbandyan, see Ref. 92, p. 140.
99. E. B. Gordon, A. N. Ponomarev, and V. L. Tal'roze, Khim. Vysok. Energii, 2, 512 (1968).
100. V. L. Tal'roze, A. N. Ponomarev, A. F. Dodonov, and E. B. Gordon, see Ref. 92, p. 13.
101. I. N. Marov, V. K. Belyaeva, A. N. Ermakov, and Yu. N. Dubrov, Zhur. Neorg. Khim., 14, 2640 (1969) [Russ. J. Inorg. Chem., No. 10 (1969)].
102. V. P. Sazonov, E. A. Sokolov, V. A. Benderskii, B. V. Ozherel'ev, and G. R. Trubnikov, Otkrytiya, Izobreteniya, Promyshlennye Obraztsy i Tovarnye Znaki, No. 32, 124 (1972).
103. B. N. Provotorov, Zhur. Eksper. Teor. Fiz., 42, 882 (1962).
104. I. V. Aleksandrov, "Teoriya Yadernogo Magnitnogo Rezonansa" (Theory of Nuclear Magnetic Resonance), Fizmatizdat, Moscow, 1964.
105. A. N. Nesmeyanov, "Periodicheskaya Sistema Elementov D. I. Mendeleeva i Organicheskaya Khimiya (Doklady na VIII Mendeleevskom S'ezde po Obshchei i Prikladnoi Khimii)" (Mendeleev's Periodic System of the Elements and Organic Chemistry—Lectures at the Eighth Mendeleev Congress of General and Applied Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1959.
106. A. N. Nesmeyanov, E. I. Fedin, L. A. Fedorov, and P. V. Petrovskii, Zhur. Strukt. Khim., 13, 1033 (1972).
107. A. N. Nesmeyanov, P. V. Petrovskii, L. A. Fedorov, V. I. Robas, and E. I. Fedin, Zhur. Strukt. Khim., 14, 49 (1973).
108. D. N. Kursanov, Z. N. Parnes, N. M. Loim, N. E. Kolobova, I. B. Zlotina, P. V. Petrovskii, and E. I. Fedin, J. Organometallic Chem., 44, C-15 (1972); 52, C-33 (1973).
109. V. I. Sokolov, P. V. Petrovskii, A. A. Koridze, and O. A. Reutov, J. Organometallic Chem., 76, C-15 (1974).
110. L. L. Morozov, E. I. Fedin, and M. I. Kabachnik, Zhur. Fiz. Khim., 47, 1992, 2000, 2012 (1973) [Russ. J. Phys. Chem., No. 8 (1973)].
111. M. I. Kabachnik, E. I. Fedin, L. L. Morozov, T. A. Mastryukova, A. E. Shipov, M. S. Vaisberg, and P. V. Petrovskii, Dokl. Akad. Nauk SSSR, 215, 1153, 1400 (1974).
112. Yu. S. Konstantinov, "Trudy I Konferentsii po Magnitnomu Rezonansu" (Proceedings of the First Conference on Magnetic Resonance), Kazan, 1959.
113. I. L. Knunyants, Yu. S. Konstantinov, B. L. Dyatkin, E. P. Mochalina, and S. R. Sterlin, Izv. Akad. Nauk SSSR, Ser. Khim., 2297 (1967).
114. K. A. Andrianov, E. I. Fedin, I. A. Lavygin, N. V. Gorskaya, and B. D. Lavrukhin, Dokl. Akad. Nauk SSSR, 166, 349 (1966).
115. K. A. Andrianov, A. A. Zhdanov, B. D. Lavrukhin, M. M. Levitskii, and E. I. Fedin, Dokl. Akad. Nauk SSSR, 182, 97 (1968).
116. K. A. Andrianov, N. A. Kurasheva, B. D. Lavrukhin, and L. I. Kuteinikova, Vysokomol. Soed., 14A, 2450 (1972).
117. K. A. Andrianov, B. D. Lavrukhin, T. B. Biryukova, B. G. Zavin, and V. S. Svistunov, Dokl. Akad. Nauk SSSR, 207, 1113 (1972).
118. V. F. Bystrov, V. T. Ivanov, S. A. Koz'min, I. I. Mikhaleva, K. Kh. Khalilulina, Yu. A. Ovchinnikov, E. I. Fedin, and P. V. Petrovskii, FEBS Letters, 21, 34 (1972).
119. G. K. Semin and E. I. Fedin, Zhur. Strukt. Khim., 1, 252, 454 (1960).
120. G. K. Semin, T. A. Babushkina, and G. G. Yakobson, "Primenenie Yadernogo Kvadrupol'nogo Rezonansa v Khimii" (Application of Nuclear Quadrupole Resonance in Chemistry), Leningrad, 1972.
121. B. A. Arbuzov, V. G. Vul'fson, I. A. Safin, I. P. Biryukov, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1243 (1970).
122. M. G. Voronkov, I. P. Biryukov, and I. A. Safin, "Tablitsy Chastot YaKR" (Tables of Nuclear Quadrupole Resonance Frequencies), Khimiya, Moscow, 1970.
122a. Vestnik Akad. Nauk SSSR, No. 4, 44 (1966).
123. R. Herber and S. Chandra, J. Chem. Phys., 52, 6045 (1970).
124. H. Thrane and G. Trumpy, Phys. Rev. (B), 1, 153 (1970).
125. R. Herber, S. Chandra, and Y. Hazony, J. Chem. Phys., 53, 3330 (1971).
126. R. Herber and S. Chandra, J. Chem. Phys., 54, 1847 (1971).
127. I. P. Suzdalev and E. F. Makarov, "Proceedings of the Conference on the Applications of the Mössbauer Effect", Akademiai Kiado, Budapest, 1971, p. 221.
128. N. Malathi and S. P. Puri, Chem. Phys. Letters, 10, 154 (1971).
129. H. D. Pfannes and U. Gonser, Appl. Phys., 1, 93 (1973).
130. H. Armon, E. Bauminger, A. Diamant, I. Nowik, and S. Ofer, Phys. Letters, 44 (A), 279 (1973); Solid State Comm., 15, 543 (1974).
131. G. Shenoy and J. Friedt, Phys. Rev. Letters, 31, 419 (1973).
132. A. Gedikli, H. Winkler, and E. Gerdau, Z. Physik, 267, 61 (1974).

133. V.I. Gol'danskii and L.A. Korytko, Pis'ma Zhur. Eksper. Teor. Fiz., 17, 312 (1973).
134. B.V. Borshagovskii, V.I. Gol'danskii, G.B. Seifer, and R.A. Stukan, Izv. Akad. Nauk SSSR, Ser. Khim., 1016 (1971).
135. V.P. Alekseev, V.I. Gol'danskii, V.E. Prusakov, A.V. Nefed'ev, and R.A. Stukan, Pis'ma Zhur. Eksper. Teor. Fiz., 16, 65 (1972).
136. G.R. Kalamkarov, V.E. Prusakov, M.A. Ostrovskii, R.A. Stukan, and V.I. Gol'danskii, Dokl. Akad. Nauk SSSR, in the press.
137. V.I. Gol'danskii and Yu. Kagan, Uspekhi Fiz. Nauk, 110, 445 (1973); Zhur. Eksper. Teor. Fiz., 64, 90 (1973).
138. Yu.A. Il'inskii and R.V. Khokhlov, Uspekhi Fiz. Nauk, 110, 449 (1973).
139. V.S. Letokhov, Zhur. Eksper. Teor. Fiz., 64, 1555 (1973).
140. V.I. Nefedov, "Primenenie Rentgenoelektronnoi Spektroskopii v Khimii" (Application of X-Ray Electron Spectroscopy in Chemistry), "Itogi Nauki" (Results of Science), Izd. VINITI, Moscow, 1973.
141. A.P. Vinogradov, V.I. Nefedov, V.S. Urusov, and N.M. Zhavoronkov, Dokl. Akad. Nauk SSSR, 201, 957 (1971).
142. V.I. Nefedov, V.S. Urusov, and N.M. Zhavoronkov, Dokl. Akad. Nauk SSSR, 207, 698 (1972).
143. V.I. Nefedov, Yu.A. Buslaev, N.P. Sergushin, and L. Boyer, Izv. Akad. Nauk SSSR, Ser. Fiz., 38, 456 (1974).
144. M. Dyatkina, Proc. Thirteenth Internat. Conf. Coordination Chemistry, Poland, Sept. 1970, p. 19.
145. A.T. Shuvaev, Izv. Akad. Nauk SSSR, Ser. Fiz., 28, 758 (1964).
146. V.I. Nefedov, Zhur. Strukt. Khim., 13, 352 (1972).
147. A.V. Nikolaev, A.P. Sadovskii, L.N. Mazalov, G.N. Dolenko, and E.S. Gluskin, Dokl. Akad. Nauk SSSR, 212, 1149 (1973).
148. S.A. Nemnonov, E.Z. Kurmaev, and V.I. Minin, in "Rentgenovskie Spektry i Elektronnaya Struktura Veshchestva" (X-Ray Spectra and the Electronic Structure of Matter), Izd. Inst. Metallofiz. Akad. Nauk Ukrain. SSR, Kiev, 1969, Vol. 1, p. 87.
149. V.V. Nemoshkalenko, "Rentgenovskie Emissionnye Spektry Metallov i Splavov" (X-Ray Emission Spectra of Metals and Alloys), Naukova Dumka, Kiev, 1972.
150. Ya.K. Syrkin and M.E. Dyatkina, "Khimicheskaya Svyaz' i Stroenie Molekul" (The Chemical Bond and the Structure of Molecules), Moscow, 1946.
151. Ya.K. Syrkin, Uspekhi Khim., 31, 397 (1962) [Russ. Chem. Rev., No. 4 (1962)].
152. E.M. Shustorovich, "Khimicheskaya Svyaz'" (The Chemical Bond), Nauka, Moscow, 1973.
153. L.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.
154. E.M. Shustorovich and M.E. Dyatkina, Dokl. Akad. Nauk SSSR, 128, 1234 (1959); 131, 113 (1960); 133, 141 (1960).
155. E.M. Shustorovich and M.E. Dyatkina, Zhur. Strukt. Khim., 1, 109 (1960); 2, 49 (1961).
156. A.A. Levin, "Vvedenie v Kvantovuyu Khimiyu Tverdogo Tela" (Introduction to the Quantum Chemistry of the Solid State), Khimiya, Moscow, 1974.
157. Ya.K. Syrkin, see Ref. 18, p. 85.

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