

The interplay of nuclear and chemical physics¹⁾

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A review is given of the interplay of ideas and methods used in the study of the structure of matter at the four main conceptual levels of chemistry and physics, i.e., elementary particles, nuclei, atoms, and molecules. Examples are quoted of new achievements in the study of radioactivity, including the formation and properties of the heaviest elements and "new atoms" in which the proton or electron is replaced by a different elementary particle. Emphasis is placed on the importance of hyperfine interactions between the nucleus and the atomic shell electrons, and between inner and valence shells, which form the basis of most modern experimental methods in chemical physics. The possible interrelation between dissymmetry in the bioorganic world and the nonconservation of parity in weak interactions is discussed in the light of new experimental work in this field. This suggests that one of the main problems in chemical and biochemical physics is the acquisition of dynamic structural data on the properties of molecules, i.e., the establishment of a connection between changes in the electron structure of molecules and their functional motion.

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For a very long time, there has been a tacit acceptance of a peculiar hierarchy in natural sciences. In the sequence mathematics-physics-chemistry-biology, the "higher" sciences were supposed to enrich the "lower" sciences with their methods and ideas, thus stimulating their further development.

One of the clearest examples of a violation of this alleged hierarchy, which illustrates the enormous and highly penetrating influence of a discovery in chemistry on the development of physics, was the renaissance of theoretical ideas and experimental methods in the study of the structure of matter, following the discovery of the periodic law by D. I. Mendeleev.

Mendeleev had the good fortune to enjoy worldwide recognition in his own lifetime. But the enormous significance of his main achievement—the periodic law—was fully recognized only by the succeeding generations.

The discovery of the atomic nucleus by Rutherford, and investigations of the x-ray spectra by Moseley, revealed the physical significance of the position number of an element in the Mendeleev system, and led to the interpretation of this number as a measure of the positive charge carried by the nuclei of the atoms of this element. Bohr's theory then related the planetary model of the atom to quantum theory, and gave a theoretical interpretation of the periodicity in the chemical properties of elements, thus providing a means of predicting the structure of the sixth period in the Mendeleev system, and the properties of hafnium and rhenium, which had not been known at the time. However, the

particular and exceedingly important consequence of the comparison between the periodic system and quantum theory was the exclusion principle put forward by Pauli in 1925. From Mendeleev's work, through Pauli's principle, and on to the Fermi-Dirac statistics, we see clear progress toward the theory of all the varied phenomena connected with the particular properties of fermions, including the theory of chemical bonds, atomic nuclei, metals, and semiconductors.

Thus, the interface between physics and chemistry was the place of origin and rapid development of the modern science of the structure of matter which, in the last twenty years, has found a fundamentally new application in molecular biology.

It is possible to identify four main conceptual classes or levels of investigation among physical and chemical problems in the structure of matter. They are: elementary particles, nuclei, atoms, and molecules.

Until quite recently, there was a relatively clear distribution of these four classes between physics and chemistry. Elementary particles and nuclei, and the interiors of atoms and molecules, i.e., the inner electron shells, were the property of physics. Chemistry, on the other hand, was occupied with the behaviour of the outer (i.e., valence) electron shells, which determined the reactivity of atoms and molecules, and studied the formation of and changes in the bonding between them, as well as the rates and equilibria of the associated processes.

However, perhaps the most characteristic feature of the modern science of the structure of matter is the overlap and mutual interpenetration of the above four fundamental levels of study, which have led to a mutual enrichment with ideas, methods, and theories. Nuclear chemistry and the chemistry of elementary particles have emerged, and the so-called hyperfine interactions have been discovered and have become the basis of many modern experimental methods of studying the structure of matter.

Chemical structure and kinetic studies have been

¹⁾This paper reproduces in its main features the text of a lecture given by the author to a special meeting of the Scientific Council of the Institute of Chemical Physics of the Academy of Sciences of the USSR, which was held to celebrate the 250th Anniversary of the Academy of Sciences. The aim of the lecture was not to provide a comprehensive review of the most topical problems in the structure of matter but merely to analyze some new possibilities and problems which have arisen on the interface between nuclear and chemical physics. The various examples and illustrations were chosen largely from Soviet literature.

greatly enriched by contact with new branches of physics such as microwave spectroscopy, quantum electronics, and cryogenics, and by the application of nuclear instrumentation and equipment.

At the same time, much of the progress achieved in nuclear and elementary-particle physics has been due to the use of analogies with the properties of atoms and molecules, based on the Mendeleev method borrowed from chemistry.

The last decade has been distinguished not only by the discovery of a large number of new elementary particles, but also by the first major successes in the systematization of their properties, and the prediction of new particles on this basis. Murray Gell-Mann (USA), the author of the first systematics of elementary particles, based on the new quantum number known as strangeness and on the utilization of group-theoretic ideas, has explicitly indicated the analogy between his work and the Mendeleev discovery of regularities in the properties of chemical elements. He has suggested that a theory of these particles capable of explaining their interactions may well develop in the future in a way similar to that in which Pauli's principle and quantum mechanics have evolved and provided an explanation of regularities in the properties of atomic systems discovered by Mendeleev.

An even more direct connection of this kind can be seen in recent elementary-particle physics, where mesons are treated as quasiautomic systems, and baryons such as protons and neutrons are regarded as quasimolecules consisting, respectively, of two and three particles with fractional electric charge, i.e., the so-called quarks.

Several new elementary particles (mesons) were discovered in the course of the last year, both in the Soviet Union (by the group directed by Yu. D. Prokoshkin, working on the Serpukhov accelerator) and elsewhere. Some of the properties of the newly discovered mesons can be described by analogy with the lightest of all known atoms, i.e., the atom of positronium, to which we shall return later, with the special difference that positronium consists of a positron and an electron, i.e., particles which are well known in their free state, whereas the new mesons consist of "charmed" particles (the language of modern elementary particles is frequently quite poetic), i.e., the quark and the antiquark, which so far have not been seen in their "pure" form.

Other new facts in elementary-particle physics have been successfully interpreted in terms of an atomic-type model consisting of a nucleon and an antinucleon, which was proposed at the Institute of Theoretical and Experimental Physics in Moscow (I. S. Shapiro). Thus, for example, one can imagine an ordinary atom of hydrogen in which the electron has been replaced by an antiproton, so that the interaction between the two particles involves not only electrostatic (i.e., Coulomb) forces, but also nuclear forces which are stronger by several orders of magnitude. Such a quasiautom can exist, just like the usual hydrogen atom, in a whole series of discrete excited states capable of deexcitation

through the emission of high-energy gamma rays.

A striking example of the application of atomic and molecular ideas to elementary particles is the prediction and discovery in the Soviet Union of the electromagnetic polarizability of elementary particles, i.e., the ability of these apparently basic building blocks to deform under the action of external electric and magnetic fields and to assume induced (dynamic) electric and magnetic dipole moments. This is, of course, a commonplace phenomenon in the physical chemistry of molecules, but the possibility of demonstrating it in the case of elementary particles was first analyzed in detail, taking the proton as an example, by theoreticians at the Lebedev Physics Institute (A. M. Baldin and V. A. Petrun'kin) and at the Joint Institute for Nuclear Research in Dubna (V. S. Barashenkov, L. I. Lapidus, and V. K. Fedyanin) in the late fifties and early sixties. The electric and magnetic polarizability of the proton was discovered experimentally by O. A. Karpukhin, A. V. Kutsenko, V. V. Pavlovskaya, and the present author in 1960 as a result of experiments performed on the 265-MeV synchrotron of the Lebedev Institute, in which the Compton effect on the proton was investigated. In 1974, a new major series of precision experiments in this field was completed at the Lebedev Institute (by P. A. Baranov, G. A. Sokol, L. N. Shtarkov, *et al.*). It was shown that elementary particles had electric and magnetic polarizabilities as fundamental physical constants which were also calculated, taking the proton as an example. This served as further evidence for the fact that elementary particles were not structureless objects, but were complicated, spatially extended, and dynamically deformable systems.

Passing from elementary particles to atomic nuclei, we again see the continuation of the Mendeleev method of systematization of elements in the highly successful and generally accepted nuclear systematics based on the existence of a large number of neutron and proton shells in nuclei. It is important to recall that the formulation and development of the shell model were due to developments in the study of radioactivity and, in particular, the phenomenon of isomerism of artificially radioactive isotopes, discovered in 1935 in the USSR by I. V. Kurchatov *et al.*, and the discovery of the so-called islands of isomerism near magic values of the number of protons (Z) and neutrons (N) in nuclei.

Soviet scientists have made very major contributions to the study of radioactivity. It is well known that, of all the currently known or proposed basic types of elementary radioactive decay, only two, namely, alpha and beta (β^-) decays, were known at the end of the nineteenth and the beginning of the twentieth century. Two further types of beta decay, i.e., β^+ decay and electron capture, were discovered in the 1930's. The third type, i.e., spontaneous fission, was discovered in 1940 in the USSR by K. A. Petrzhak and G. N. Flerov. The fourth type, i.e., proton radioactivity, was suggested initially by Rutherford, but a modern prediction was not forthcoming until the 1950's. It was made by B. S. Dzhelepov *et al.* in the Soviet Union and was discovered experimentally in 1970 in the USA in the case of an

isomer of cobalt-53. Two further types of spontaneous decay of nuclei, i. e., two-proton and two-neutron radioactivity, were also theoretically predicted and described in detail for the first time in our country (in 1960 and 1971, respectively) although they have not as yet been observed. (In many world laboratories, where nuclei with high deficiency or surplus of neutrons are being investigated, the expected limits of these phenomena are rapidly being approached.) Our prediction of the possibility of the above two types of radioactive decay, i. e., the ability of a number of nuclei to emit a pair of protons or neutrons with opposite spins, but not single nucleons, has a chemical analogy in the formation of coordinate bonds in which, as is well known, one of the atoms provides a pair of electrons.

There are also predictions of a number of two-stage radioactive processes in which the first stage is some variant of beta decay and the second follows almost instantaneously and involves the emission of a particle from the excited intermediate nucleus, or the fission of the nucleus. Such processes, and the particles emitted in them, are called delayed processes, where the "delay" is due to the slow character of the first event (beta decay), i. e., not to the decay of the excited nucleus but its formation.

Soviet scientists have made major contributions to the study of delayed radioactive processes.

Only delayed alpha particles and neutrons were known prior to the research carried out by Soviet scientists. In the Laboratory for Nuclear Reactions of the Joint Institute for Nuclear Research at Dubna, V. A. Karnaukhov *et al.* discovered in 1962 the emission of delayed protons and, a few years later, G. N. Flerov *et al.* discovered delayed fission, i. e., fission following beta decay. Scientists working at the Konstantinov Institute for Nuclear Physics in Leningrad predicted two further possible two-stage radioactive processes, namely, the emission of delayed tritium and helium-3 nuclei for which an experimental search is now in progress.

About 2000 isotopes of 106 chemical elements are now known, of which only 15% are stable. However, the systematics of nucleon binding energies leads to the conclusion that a further 4000 radioactive isotopes with a strong deficit or surplus of neutrons should exist. Such isotopes are of particular interest not only in themselves, but also because they may exhibit fundamentally new properties and phenomena which will have to be investigated.

The current stage of searches for and investigations of isotopes with neutron deficiency or excess began in 1959-1960 when Soviet scientists (Ya. B. Zel'dovich, A. I. Baz', and the present author) proposed very simple and not very accurate methods of determining the limits of stability of nuclei based on the shell model and one of the basic properties of nuclear forces, namely, their charge independence. Since then, both Soviet and other scientists have found many tens of new isotopes of even the lightest elements, and their properties have turned out to be in excellent agreement with these predictions. I would like to mention here a particularly

interesting example. This is the prediction of the existence and properties of superheavy helium He^8 , which is heavier than ordinary helium by a factor of two. The formation and decay of this isotope were observed directly in photographic emulsions in the Laboratory for Nuclear Problems of the Joint Institute for Nuclear Research in Dubna by V. M. Sidorov, V. A. Yarba, *et al.* He^8 holds a kind of record among atomic nuclei in the sense that three neutrons correspond to each of its protons. Each atom of superheavy helium transforms into two atoms of ordinary helium through three successive radioactive transformations, namely, two beta and one alpha decays.

Apart from searches for new radioactive isotopes, the most popular topic in nuclear physics has been the synthesis of new transuranic elements, which has very substantially extended the periodic table.

It is well known that the first transuranic element, neptunium, was synthesized in 1940, and the fundamental contribution to the extension of the Mendeleev system was made by a group of scientists at the Lawrence Radiation Laboratory at Berkeley in the USA, led by G. T. Seaborg.

In addition to the discovery of plutonium, which was marked by the award of a Nobel Prize, this group was also responsible for the synthesis of the first element of the "second hundred," i. e., element 101, which was named mendelevium by the American scientists "... as a sign of an acknowledgment of the priority of the great Russian chemist, Dmitrii Mendeleev...," whose Periodic Law was the "key to the discovery of practically all the transuranic elements."

At the beginning of the 1960's, the laboratory headed by G. N. Flerov in Dubna, which became a virtual factory of discoveries, occupied a preeminent place among the leading centers concerned with the synthesis and properties of transuranic elements. The work of this laboratory (Laboratory for Nuclear Reactions of the Joint Institute for Nuclear Research) led to a review of the mass numbers assigned previously at Berkeley to a number of isotopes of elements 102 and 103, and this enabled the Dubna scientists to reopen the question of priority in the discovery of these two elements. In 1964, a new and remarkable achievement of the Laboratory for Nuclear Reactions of the Joint Institute for Nuclear Research was reported, namely, the discovery of the first isotopes of the next element, i. e., element 104, which was named kurchatovium (Ku) in honor of I. V. Kurchatov. The synthesis in Dubna of another element, element 105, was announced in February 1970. This was named nielsbohrium (Ns). Finally, in July 1974, it became known that element 106 was synthesized in Dubna. A number of other isotopes of elements 104-106 were synthesized subsequently in Berkeley.

At present, the Laboratory for Nuclear Reactions of the Joint Institute for Nuclear Research has to its credit sixteen isotopes of elements 102-106, for which the currently accepted parameters were first found at Dubna. They include the first isotopes of these five new elements whose properties were not subsequently re-

vised (mass numbers, respectively, equal to 256, 256, 260, 261, and 259 for $Z=102-106$). It is also important to emphasize that the nuclear properties of kurchatovium and of element 106, which were established in this laboratory, turned out to be essentially different from those expected from previously accepted systematics of spontaneous fission of heavy nuclei. This led to a revision of this systematics and provided a new stimulus to searches for further transuranic elements.

Let us now consider, if only briefly, the chemical properties of the new elements that are of main interest for chemists.

The factors that influence the actual properties of elements in chemical compounds, e.g., the degree of stability of their different valence states, are very varied. Model calculations are hardly capable of resolving this problem. In real solutions and solid compounds, one must also take into account solvation energy and the interionic and intermolecular interactions. For radioelements, the various effects of autoradiolysis are also important. Here, experiments play a decisive role: they must prepare the ground for future calculations, and any new and, especially, unexpected facts provide the foundation for theoretical generalizations.

The experiments of the Dubna radiochemists (Ivo Zvara and his collaborators) have become widely known. They have shown, using their own rapid experimental procedures that involve only tens of atoms of kurchatovium and nielsbohrium, that the chemical properties of these elements are analogous to those of hafnium and tantalum and that, in accordance with the actinide theory of Seaborg, element 103 completes the filling of the fourteen-electron $5f$ shell. There is also considerable interest in any differences between the properties of the actinides and lanthanides, which are of great importance for the chemistry of transuranic elements. These elements have been studied for the last eight or nine years at the Institute of Physical Chemistry of the USSR Academy of Sciences, and this has led to the discovery of extremal valence states of the heptavalent neptunium, plutonium, and americium (A. D. Gel'man, N. N. Krot, *et al.*), the divalent californium and einsteinium, and the monovalent mendelevium (V. I. Spitsyn, N. B. Mikheev, *et al.*). These results indicate a definite similarity between the distant actinides and the transition d -elements, suggesting that it may be possible to discover octavalent plutonium, pentavalent and hexavalent curium, and pentavalent berkelium.

Successes in the synthesis and investigation of the properties of distant transuranic elements have led to increased interest in the limits to which the periodic system can be extended. Only ten years ago, it was considered that spontaneous fission would restrict the synthesis of elements to $Z \approx 110-112$. However, calculations of both Soviet (V. M. Strutinskii) and other nuclear theoreticians have shown the possibility of enhanced stability due to the filling of nuclear shells in nuclei containing 114, 126, and 164 protons, and 184 and 258 neutrons. It turns out that there may be a peculiar stability peninsula containing many isotopes of

elements in the neighborhood of the 114, 126, and perhaps even 164 cell of the Mendeleev system.

The question is—what are the expected chemical properties of these elements? If we use the data on known elements, and extrapolate them to higher atomic numbers, we are led to the conclusion that element 114 lies near the end of the seventh period, and element 164 near the end of the eighth period. They are both analogs of lead. Element 126 is among the first group of 18 elements in the 50-element eighth period. This is the "octadecanide" group, the members of which are probably similar to actinium. The $5g$ shell is expected to become filled in these atoms.

In recent years, there have been determined attempts both in the Soviet Union and elsewhere to discover in nature, or produce in accelerators, some of the ultra-heavy elements. So far, the results have not been sufficiently conclusive. Nevertheless, the recently established links between the chemistry and physics of elementary particles have revealed quite new possibilities for the enrichment and extension of our ideas about chemical elements through the so-called "new atoms" in which the proton is replaced by another positive particle, and the electron is replaced by another negative particle. The best known "new atom" is the lightest of all the conceivable isotopes of hydrogen, namely, positronium (chemical symbol Ps). It consists of a positron and an electron, and is lighter than hydrogen by a factor of 920. Since the positron and electron masses are equal, positronium is the only atom without a heavy nucleus. All the characteristics of its decay, which is governed by the mutual annihilation of the positron and the electron, depend on the properties of the ambient medium, and this provides a completely new way of investigating these properties. The negligible lifetime of positronium ($10^{-10}-10^{-7}$ sec) means that it cannot accumulate to densities in excess of a few atoms per cubic centimeter and, therefore, none of the classical methods known in chemistry can be used to investigate positronium reactions. This can be done only by nuclear methods capable of recording the formation and disappearance of each single atom of positronium through the detection of the corresponding gamma rays. By using a combination of such methods in conjunction with widely varying external conditions (composition of the medium, density, temperature, pressure, etc.), the Institute of Chemical Physics of the USSR Academy of Sciences has been able, in the course of the last twelve years, to carry out a quantitative investigation of all the classes of chemical reactions involving positronium, including oxidation, donor-acceptor interactions, substitution, association, and conversion. Thus, for the first time in the history of radiochemistry, it has been possible to carry out a detailed study of the chemistry of atoms with lifetimes less than 10^{-7} sec, including the kinetics and the mechanism of reactions involving these atoms. However, with all the intrinsic interest in the chemistry of positronium, even more interesting for chemistry as a whole are the results obtained by the new positronium method. Thus, it has been possible to determine the rates of a number of ultrafast chemical reactions oc-

curing in a time of the order of 10^{-9} sec, and lifetimes of intermediate products of the order of 10^{-12} sec. It has also been possible to develop a method for separating kinetic and diffusion factors in the kinetics of liquid-phase reactions, to establish general results about the mechanism responsible for electron transfer during oxidation by ions of variable valence in solution, and to determine the electronic conductivity of various groups in comparison with the conductivity of the benzene ring.

The major advantage of positronium methods in structural chemistry is that they can be used to determine the momentum distribution of electrons in atoms and molecules (especially the valence electrons) from the shape of the angular and energy distributions of annihilation gamma rays. This is true both for ordinary chemical bonds, where the positron is simply a probe used to investigate the bond, and special bonds in which the positron is intimately involved. Researches carried out at the Institute of Physical Chemistry of the USSR Academy of Sciences have shown, for example, that it is possible to produce positron bonds between two helium atoms, with anions, neutral atoms, and molecules, and with crystal-lattice defects.

The ingenious method of quasielastic electron scattering (e , $2e$ method) has recently been proposed by V. G. Neudachnyi and Yu. F. Smirnov (Moscow State University) and has already been successfully tested in practice. In this method, the specimens under investigation are bombarded by slow monochromatic electrons, and measurements are made of both the angles between the scattered and ejected electrons and of the kinetic energies of the electrons. This procedure is methodologically similar to precision observations of the angles of emission and the energies of annihilation gamma rays, and is very promising for quantum chemistry.

This method is perhaps the most informative insofar as the geometry and energetics of chemical bonds are concerned, and is effective in identifying the electron shells which participate in the formation of valence bonds and the degree of this participation, i.e., the data forming the experimental foundation of structural quantum chemistry.

Positronium chemistry has emerged from the "testing" stage and has become the source of new and valuable chemical information. The chemistry of other new atoms, occasionally called mesochemistry, is still in its early stages of development. Nevertheless, even the results obtained so far are very promising. The pioneering work in the field of mesochemistry has been carried out on the synchrocyclotron of the Laboratory for Nuclear Problems of the Joint Institute for Nuclear Research in Dubna both by the staff of the laboratory itself (Yu. D. Prokoshkin, A. I. Mukhin, V. G. Zinov, V. S. Evseev, *et al.*) and by workers from other institutes (I. I. Gurevich, B. A. Nikol'skii, *et al.* from the Kurchatov Institute of Atomic Energy and by V. G. Firsov *et al.* from the Institute of Theoretical and Experimental Physics, and B. V. Kirillov-Ugryumov, B. A. Dolgoshein *et al.* from the Moscow Engineering-Physics Institute).

Observations of the formation and transformation of mesomolecules have resulted in the well-known "large mesomolecule model" (L. I. Ponomarev), and have led to a number of conclusions with regard to the properties of valence bonds in these molecules and the electronic effects of the different functional groups. Such observations can also be used to establish a definite correlation between mesochemical and radiochemical reactions, and to determine the rate of chemical reactions involving the participation of mesoatoms and mesoradicals.

We have already frequently mentioned the four conceptual levels at which the structure of matter can be investigated, and have examined the sequence particles-nuclei-atoms-molecules. However, the proper path for modern studies must be based on a synthesis of the ideas on the structure of nuclei and electronic shells, and the underlying unity of the quantum-mechanical description of the properties of both.

The discovery and interpretation of Mendeleev's periodic law have provided chemistry and physics with two types of dependence of the properties of electron shells on nuclear charge. Thus, for the outer, i.e., valence shells, we have a periodic relationship which is known to hold, for example, for atomic volumes. In the case of the inner shells, we have a monotonic power-law dependence, a well-known example of which is Moseley's law.

The next, contemporary, stage to which Soviet scientists have contributed enormously is characterized by the discovery, investigation, and application in chemistry and in other natural sciences of the interactions between the outer and inner electrons, and between the outer electrons and nuclei, i.e., the connection between the periodic and the monotonic functions of the atomic number (in special cases, the atomic number Z itself).

The first example of such interactions, now combined under the common name of hyperfine interactions, was discovered in 1928 by A. N. Terenin and L. N. Dobretsov in the USSR and, independently, by H. Schuler in Germany, as a result of precision studies of the optical spectra of sodium vapor.

One of the main forms of hyperfine interaction is the interaction between the electric monopole, magnetic dipole, and electric quadrupole moments of nuclei, on the one hand, and the electron charges, the intramolecular magnetic field, and the inhomogeneous intramolecular electric field, on the other. These hyperfine interactions are used in electron spin resonance and in other methods of microwave spectroscopy, including, in particular, nuclear magnetic and nuclear quadrupole resonance. Hyperfine interactions play the decisive role in Mössbauer spectroscopy, which has been placed at the service of chemistry as a result of the work of Soviet scientists. In all cases, the energy of the hyperfine interaction between nuclei and valence electrons is several orders smaller than the energy associated with even the strongest chemical bonds.

The interaction between the electric charges in outer and inner electron shells is reflected in the changes, by

fractions of an electron-volt or even a few electron-volts, in the energy of electrons ejected from inner shells of atoms, and leads to the appearance of a specific fine structure on x-ray spectra.

This is the basis for the so-called photoelectron spectroscopy, the x-ray variant of which was developed by K. Siegbahn *et al.* in Sweden²⁾ and the ultraviolet variant by A. N. Terenin *et al.* in the USSR. It is also the basis for precision x-ray chemical spectroscopy developed by the staff of the USSR Academy of Sciences at the Veradskii Institute of Geochemistry and Analytical Chemistry (É. E. Vainšteĭn), the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements (R. L. Barinskii), the Kurnakov Institute of General and Inorganic Chemistry (V. I. Nefedov), and particularly successfully in recent years at the Konstantinov Leningrad Institute for Nuclear Physics (O. I. Sumbaev). O. I. Sumbaev has substantially increased the accuracy of the last method and has developed it so that it can be used even for heavy elements.

Let us now consider some examples of the major successes of Soviet scientists in the utilization of hyperfine interactions in different branches of chemistry.

We shall begin with electron paramagnetic resonance which itself was discovered in the Soviet Union by E. K. Zavoiskii in Kazan in 1944, for which, four years later, S. A. Al'tshuler and B. M. Kozyrev were the first to observe the hyperfine structure.

It is well known that the development of chemical ESR spectroscopy is, in many ways, due to V. V. Voevodskii, who developed it to the point where it became a powerful tool for structural-kinetic studies and, in particular, for the observation of free radicals, formed directly during the irradiation of various materials, and the so-called chemically weak interactions, the energy of which is very much smaller than ordinary thermal energy, but is close to the energy of the hyperfine interactions. Such interactions are too weak for observation by optical spectroscopy, measurements of dipole moments, and so on, but they nevertheless frequently determine important physical phenomena (such as the mutual influence of the reactivities of spatially separated and different functional groups) and are reflected in the different (in space and time) delocalization of electrons and molecules. ESR has been used for direct observation of such delocalization, i. e., electron exchange between distant but identical functional groups, in the case of the stable nitric oxide diradical in which the frequency of this exchange exceeds 10^8 – 10^9 sec⁻¹.

Other interesting recent applications of ESR in chemistry include direct observation of the tunneling of electrons at low temperatures when the tunneling distance is of the order of a few tens of angstroms. The kinetic-recombination method used in conjunction with ESR has resulted in the observation of exceedingly slow motions of paramagnetic centers with linear velocities of 10^{-7} cm/sec and diffusion coefficients down to

10^{-17} – 10^{-18} cm²/sec.

Nuclear magnetic resonance has been exceptionally widely used by Soviet chemists, and Soviet scientists have made fundamental contributions to the theoretical foundations of the new method. The world-famous work of B. N. Provotorov has combined ideas on spin temperature and the reservoir of dipole-dipole interactions, and has led to general equations describing transformations in nuclear-spin systems for arbitrary values of the saturated field.

The standard text for NMR specialists is the book by I. B. Aleksandrov, "Theory of Nuclear Magnetic Resonance," which gives the complete theory of the magnetic shielding of nuclei.

NMR has of recent years found very fruitful applications at the Institute for Elementoorganic Compounds of the USSR Academy of Sciences, where it is being applied to the interesting problem of dissymmetry in the organic and bio-organic world.

I must now recall, if only in brief and simplified form, the essence of this problem. It is well known that, under the usual laboratory conditions, optically active materials are formed as mixtures of equal amounts of left-handed and right-handed (*L* and *D*) isomeric forms, i. e., the so-called racemic mixtures or racemates. In the living world, on the other hand, this situation is reversed in that the two forms are not found in equal amounts. Thus, natural proteins include only *L* isomers of optically active aminoacids, whereas natural sugars contain only the *D* isomers of asymmetric chains. The question is—what is the reason for this imbalance, and what are its possible consequences?

The discovery of this dissymmetry, and the emergence of the above problems, go back to an early period in Louis Pasteur's scientific creativity. A possible explanation has been a purely statistical hypothesis which interprets the predominance of one of the isomeric forms as being the result of mere chance, for example, the fact that the first microcrystal produced in the saturated solution (which is subsequently the center of crystallization) is levorotatory, or dextrorotatory, for polarized light.

Nearly 70 years ago, Jacobus Van't Hoff suggested the possibility of asymmetric photochemical synthesis under the action of circularly polarized light, and this was confirmed experimentally 20 years later. Dissymmetry problems occupy a prominent place in the classical papers of A. I. Oparin on the origin of life. Soviet organic chemists have been responsible for many ingenious experiments on the synthesis of optically active compounds, using asymmetric adsorbents or catalysts, and experiments on the separation of *L* and *D* isomers into optically active ion exchange.

I should now like to sketch in another important fact: nearly 20 years ago, the dissymmetry problem turned out to be a new interface between structural chemistry (especially bio-organic chemistry) and elementary-particle physics. Here again, we have a clear example and a confirmation of the interrelationship and unity of

²⁾It is commonly known as ESCA—electron spectroscopy for chemical analysis.

the various ideas on the structure of matter at different levels of complexity.

The point is that, in 1956, it was postulated theoretically and was soon confirmed experimentally that parity was not conserved in the so-called weak interactions which include beta decay. In other words, a left-right asymmetry was established, so that events and their mirror images were not equivalent for weak interactions although in strong (nuclear) and electromagnetic interactions, this effect was negligible.

Modern elementary-particle physics is characterized by relatively complicated concepts of spatial, charge, and temporal symmetry of the interactions between particles, and the connection between charge and spatial parities of particles and antiparticles. For example, the neutrino is looked upon as a kind of left-handed screw, and the antineutrino as a right-handed screw. In the same way, electrons emitted during beta decay are polarized in the direction opposite to that of their motion (left-handed screw), whereas positrons are polarized in the same direction (right-handed screw). Such properties are described by the words *chirality* or *helicity*.

However, the chirality of elementary particles can, in principle, have as a direct consequence the appearance of dissymmetry in the structure of molecules.

For example, we can imagine the following mechanism. Longitudinally polarized electrons from beta decay emit circularly polarized bremsstrahlung as they travel through space, and the spectrum of this extends into the photochemically active region. The result is the asymmetric synthesis of a type predicted by Van't Hoff. In 1959-1961, there were some published reports on the experimental confirmation of differences between the effects of beta rays on *L* and *D* optical isomers. Careful experiments performed both in the Soviet Union (at the Institute of Chemical Physics in 1962) and elsewhere did not, however, confirm this although, in principle, the effect was possible but so weak that it lay outside the range of observation.

The other possibility, first noted and analyzed in detail by Soviet theoretical physicists, is much more interesting. Nonconservation of parity in the so-called neutral weak-interaction currents, which was proposed as far back as 1959 by Ya. B. Zel'dovich, and has recently been confirmed experimentally, violates the absolute equality of the energies of the left- and right-handed forms of molecules and crystals, even in optically inactive media (including vacuum), so that an exceedingly small difference in the energy and, consequently, in the activity of optical isomers is produced. On a scale of many billions of years, such tiny differences may, in the end, lead to a very substantial imbalance between different diastereoisomers in bio-organic chemistry.

Research carried out at the Institute for Elementary Organic Compounds by the NMR method in 1972-1975 produced qualitative evidence for differences between the reactivities of even identical, optically inactive groups in the case of the general dissymmetry of mole-

cules including such groups.

A very interesting phenomenon was discovered, for example, in the laboratory directed by D. N. Kursanov. When the cyclopentadiene (*Cp*) ring



contains a substituent with a symmetric atom C_{symm} in a direct proximity of the ring, the NMR spectra of the two β -atoms of C^{13} and the two α -atoms of C^{13} are identical in pairs. However, when the *Cp* ring has in its neighborhood an asymmetric atom C_{asymm} , there are differences between the α and α' and between β and β' atoms of C^{13} . It has been possible to detect the short-range and the long-range intramolecular influences of asymmetric atoms.

In a series of papers, M. I. Kabachnik *et al.* have demonstrated still weaker effects of the differences between the intramolecular interaction of mirror antipodes. This has become possible as a result of the exceptionally high sensitivity of the NMR method and the excellent reproducibility of the results. When a solution of "left-handed" molecules of biologically active phosphoric depsipeptides in a nonactive solvent (chloroform) is examined, it is found that there is a definite chemical shift of the singlet NMR spectrum of P^{31} . Precisely the same shift is, of course, observed for a solution of "right-handed" molecules. When the left-handed and right-handed molecules are equal in number, the NMR singlet is observed, but is no longer shifted. In the general case, i. e., the case of left-right mixture, there are two NMR lines, the positions and intensities of which depend on the concentration ratios of the left-handed and right-handed forms. Thus, the "homocontacts" and "crosscontacts" of left-handed and right-handed molecules in an inert solvent are found to be different, and their mutual screening is not equivalent. A pair consisting of left- and right-handed molecules forms an associated diastereoisomer which is short-lived on the NMR time scale ($\tau \lesssim 10^{-3}$ sec).

The continuation and development of such researches is clearly of fundamental importance for a wide circle of problems in the structure of matter, ranging from elementary-particle physics to molecular biology.

Among modern methods based on the application of the hyperfine interaction to the study of the structure of matter, we must also recall the Mössbauer or gamma-resonance spectroscopy. The achievements of Soviet chemical physicists in this field include the discovery and interpretation of the asymmetry effect in Mössbauer spectra, which can be used to detect and describe quantitatively the anisotropy of bonds and vibrations of atoms, molecules, and crystals by examining the spectra of isotropic polycrystalline powders by analogy with the Debye method in x-ray crystallography, in which the structure of single crystals can be determined from experiments on powders. More than one hundred papers in Soviet and other literature have been devoted to this effect in the last few years.

Very considerable new possibilities insofar as both structural and radio-chemical information is concerned are being offered by a new variant of Mössbauer spectroscopy, namely, emission spectroscopy, in which the atoms under investigation are taken not in the stable form of absorbers, but in the radioactive form of emitters of resonance gamma rays.

It is well known that the precision of Mössbauer measurements is unrivalled; relative changes of 10^{-15} – 10^{-16} in the energy of spectral lines can be determined, which is better by five or six orders of magnitude than the relative precision of NMR. However, the nuclear-transition energies used in the Mössbauer effect are of the order of few tens of keV, which exceeds the characteristic energies involved in NMR by a factor of 10^{12} . Moreover, because of the spread in local electric and magnetic fields and the possible presence of defects, dislocations, and soon when the resonance transition involves the participation of two different nuclei (the emitter and the absorbed of gamma rays), the spectral lines are necessarily subject to strong inhomogeneous broadening. This is why it has not been possible to observe absolute Mössbauer linewidths of less than about 10^{-10} eV, which is wider by seven orders of magnitude than the narrowest NMR lines. This has been the decisive factor in the lack of success in the development of the gamma laser which was proposed more than ten years ago. However, during the last three or four years, R. V. Khokhlov, Yu. M. Kagan, and the present author have published some fundamentally new ideas, and these have led to the hope that gamma lasers based on lines with large natural widths (i. e., short-lived nuclei) and pulsed neutron pumping, and also the suppression of line broadening by a combination of Mössbauer and NMR methods, will become possible. Moreover, V. S. Letokhov (Institute of Spectroscopy of the USSR Academy of Sciences) has proposed an original laser method for the separation of nuclei excited to Mössbauer levels necessary for the emission of stimulated gamma radiation from similar nuclei in the ground state. The search for the gamma laser is exceedingly interesting for physics, chemistry, and biology in connection with the possible development of direction holographic three-dimensional imaging of molecules.

It is well known that one of the most interesting and important problems in modern physical chemistry, which is of major theoretical and applied significance, is the establishment of the connection between the structure of molecules and their reactivity. In physicochemical biology, the corresponding problem is the elucidation, at the electronic and molecular levels, of the origin and essence of what V. A. Engel'gardt generally describes as "molecular kinesis," i. e., any fundamental motion of molecules.

It is important to be able to understand how and why a change in the electron state of a particular atom may result in the participation of a molecule in a chemical reaction, a conformational transition in a molecule of a biopolymer, or the appearance of other types of motion at the molecular, supermolecular, and cell levels; what is the causal relationship, and what are the paths

and mechanisms of transfer of the signal which activates this causal relationship between the primary receiver and the receptor? Purely structural and static data are insufficient for the solution of such important problems in the structure of matter. Dynamic observations are essential. As a matter of fact, the gamma laser, or even ordinary x-ray analysis, may be particularly convenient for this purpose when exceedingly short exposures become possible through the replacement of x-ray tubes by powerful sources of synchrotron radiation.

The importance of methods based on the observation of hyperfine interactions will also substantially increase precisely because they can be used to obtain combinations of electron-structure and dynamic data. Such data can be obtained by introducing special paramagnetic traces in the form of stable radicals into the system under investigation, for example, complicated biopolymers, and observing the motion of these radicals by ESR (A. L. Buchachenko, G. I. Likhtenshtein, and É. G. Rozantsev).

NMR and Mössbauer spectroscopy—the two resonance methods mentioned above—are also capable of providing very substantial dynamic structural data.

Yu. A. Ovchinnikov *et al.* have used NMR to obtain an exceedingly clear and fundamental result which has led to an understanding of the transport of molecules of specifically complex biopolymers (the so-called ionophores) through biological membranes. Fourier spectroscopy has been used in conjunction with the NMR of C^{13} to demonstrate conformational rearrangement of the antibiotic valinomycin during complexation with a potassium cation. Complexation is accompanied by a substantial shift of the carbonyl group toward lower magnetic fields, which is explained both by the effect of hydrogen bonds and the participation of these groups themselves in the weak ion-dipole interaction which holds the cation K^+ in the closed bud-shaped structure of the valinomycin complex.

Such experiments have elucidated the competition between intra- and intermolecular hydrogen bonds which hold ions in the central cavity of these beautiful flower-like cyclic molecules, and the freeing of the ions during the conformational opening out of the bud, when the effect of the medium breaks the intramolecular hydrogen bonds. These results are particularly significant because it is these conformational changes that are responsible for important molecular biological processes such as the transport of ions through cell membranes.

Important problems in molecular biology, which are being examined at the USSR Academy of Sciences, also include studies of the mechanism responsible for the properties of photoreceptors and the effect of light on visual pigments and photoreceptor membranes (the so-called Rhodopsin Project).

A very interesting result in this field has recently been obtained at the Institute of Chemical Physics by M. A. Ostrovskii, G. R. Kalamkarov, R. A. Stukan, *et al.* with the aid of the Mössbauer effect, again as a result of the unique possibility afforded by this method

of simultaneously exhibiting both electron-structure and dynamic properties of matter.

These workers have found that even the first stage of the photolysis of the pigment, i. e., the transformation of rhodopsin into prelumorphodopsin, is accompanied not only by photoisomerization of the chromophore (II-*cis*-retinal → *trans*-retinal), but also the reversible conformational rearrangement of the entire photoreceptor membrane, which occurs even at liquid nitrogen temperatures and leads to a sharp increase in the rate of spin-lattice relaxation.

Mössbauer spectroscopy is also very promising for the observation of spatial and temporal delocalization of electrons in molecules and more complicated systems. Recently, researchers at the Institute of Chemical Physics have observed the spatial delocalization not merely of a single electron, but of an electron pair, as a result of a very rapid migration between atoms of tri- and pentavalent antimony in multifunctional compounds of this element. This type of delocalization destroys the individuality of these two atoms, since they acquire an effectively identical valence equal to four.

The combined application of emission Mössbauer spectroscopy and delayed gamma-gamma coincidences has recently led to the first direct measurements (at the Institute of Chemical Physics) of the rate of intramolecular transport of electrons in intra- and extra-spherical iron in ferri-ferrocyanide complexes. It would be very interesting to have similar observations in the case of organelles such as mitochondria and chloroplasts.

The overall aim of studies of the structure of matter in chemical and biological physics is now to obtain composite structural and dynamic information on systems

with different degrees of complexity.

Studies of this kind provide a clear demonstration of the unity and continuity of contemporary science—in the first instance, physics, chemistry, and biology—and the close interrelationship between structural ideas as applied to the entire field ranging from elementary particles to complex molecules and cells. In actual fact, developments in physics and chemistry, which have led to the discovery and interpretation of the properties of elementary particles and of the interactions between nuclei and the electron shells of atoms, form the basis for methods that can be used to investigate not only the structure of molecules but also to explain their reactivity (in other words, to solve key problems in both theoretical chemistry and chemical industry in the future) and elucidate the molecular basis of the motion of biological objects. Contrary to what is sometimes said, the role of chemistry in the triad consisting of physics, chemistry, and biology is not at all secondary. Chemistry is, in a sense, a central subject because chemical physics uses physical methods to solve chemical problems, above all problems in the structure of chemical compounds, in kinetics, and in the mechanism of chemical transformations. Having grown out of nuclear physics and electronics, chemical physics is currently undergoing a renaissance through the utilization of methods, ideas, and theories taken from elementary-particle and nuclear physics. It is clear from the foregoing examples that the achievements of chemical physics are now shared by nuclear physics, and form the basis of much successful work in biochemistry and biophysics, so that one can see the emergence of the new subject of *biochemical physics*.

Translated by S. Chomet