

Magnetic resonance: discovery, investigations, and applications

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Abstract. The history of the development of the theoretical ideas and experimental methods of magnetic resonance, as well as the applications of these methods in modern natural science, technology, and medicine, are outlined, with allowance for the contribution of Russian researchers. An assessment of some promising trends of studies and applications of magnetic resonance is given.

afraid it has little bearing on the sober question we must, as physicists, ask ourselves: What can we learn from all this about the structure of matter?

E M Purcell

Nobel lecture (December 11, 1952)

Professor Bloch has told you how one can detect the precession of the magnetic nuclei in a drop of water. Commonplace as such experiments have become in our laboratories, I have not yet lost a feeling of wonder, and of delight, that this delicate motion should reside in all the ordinary things around us, revealing itself only to him who looks for it. I remember, in the winter of our first experiments, just seven years ago, looking on snow with new eyes. There the snow lay around my doorstep—great heaps of protons quietly precessing in the earth's magnetic field. To see the world for a moment as something rich and strange is the private reward of many a discovery. But I am

1. Introduction. General characteristic of magnetic resonance methods

The subject of this article is the history of discovery and studies of magnetic resonance, some modern achievements related to these studies, and their contribution to science and technology. The number of Nobel Prizes in physics for studies (discoveries) in the field of magnetic spin resonance by 2003 became equal to the number of Nobel Prizes in physics, chemistry, and medicine for the development and realization of effective procedures for the application of magnetic resonance.¹ The methods of electronic paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and magnetic relaxation are employed in chemistry for the investigation of the molecular and supramolecular structures of matter. The structure of macroscopic objects is studied by the methods of magnetic resonance tomography [magnetic resonance imaging (MRI)]. The MRI method is indispensable in modern medicine. A unique method of magnetic-resonance force atomic spectroscopy has also found wide applications.

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¹ The list of the laureates of the corresponding Nobel Prizes with the indication of related nominations and achievements is given in the Appendix.

Many particles (leptons, including electrons; hadrons, including protons and neutrons; and atomic nuclei, free atoms, and some molecules) possess their nonzero intrinsic (spin) angular momenta and magnetic moments.² Below we will frequently name the appropriate particles simply spins or magnetic moments (of one kind or another). In the units of the Planck constant \hbar , the angular momenta of particles are expressed via the spin number S or $I \geq 1/2$. The magnetic dipole moments of these particles, μ_S or μ_I , are expressed as the product of the spin number, Planck's constant \hbar , and a dimensional factor — the gyromagnetic ratio γ_S or γ_I . Thus, one has

$$\mu_S = \gamma_S S \hbar. \quad (1.1)$$

The number of levels (eigenstates) for a system of noninteracting spins S in a magnetic field \mathbf{H}_0 or in internal fields in the substance is equal to $2S + 1$, since such is the number of spin projections on the 'quantization axis', which is parallel, for example, to the external field, $S \geq S_z \geq -S$. Transitions between the levels, which are usually accompanied by a change in the orientation of the magnetic moment by $\Delta m = \Delta S_z = \pm 1$, are caused by the magnetic component of the electromagnetic field, which rotates with a resonance frequency $\omega_0 = \gamma_S H_0$ and is perpendicular to the quantizing field. The energies of these levels do not depend explicitly on the coordinates and the momenta of the particles that are spin carriers, but only depend on the spin coordinates (projections of spins) and on the parameters of external or local interactions (for example, on the magnetic field strength). This also relates to the energy of spin systems containing different spins i, j that interact between themselves. The operators of the energy of spin systems, which are called spin Hamiltonians, have the following general form:

$$\hat{H}(S_{iz}, S_{iy}, S_{ix}; S_{jz}, S_{jy}, S_{jx}; \dots) = \sum \hat{W}_k(\mathbf{S}_i; \mathbf{S}_j; \dots). \quad (1.2)$$

Magnetic (paramagnetic, ferromagnetic, etc.) resonance represents a characteristic dependence of absorption or emission intensity on the frequency of the alternating electromagnetic field. This effect is connected with a change in the spin orientation during interaction with the magnetic component of this field.³ The appearance of an energy difference between spin sublevels (quantization) is caused by the interactions of the magnetic dipoles of electron and nuclear spins and (or) of their electrical quadrupoles⁴ with magnetic or electric fields. The difference in the energies of spin sublevels leads to the difference in the equilibrium

² The presence of 'frozen' (in a molecular or crystal field) orbital momenta in a condensed medium affects the values of magnetic moments because of spin-orbit interactions.

³ The definition 'magnetic resonance', strictly speaking, does not relate to the cyclotron, or so-called diamagnetic, resonance, in the presence of which the transitions between Landau's levels in a magnetic field occur under the action of the electrical component of the field. However, for measuring magnetic moments and, generally, for metrology, the relationship between the magnetic and cyclotron resonance frequencies is very important. Apparatuses based on the cyclotron resonance, such as the gyrotron, in particular, produced by the Bruker BioSpin Company, serve to excite and saturate EPR at frequencies on the order of 10^{12} Hz (terahertz region).

⁴ Particles with spin $S > 0$ possess magnetic dipoles; those with $S \geq 1$, electrical quadrupoles; with spins $S \geq 2$, magnetic octupoles, etc. For the nuclear spins, the energies of interaction of the octupoles and other higher moments are very small [1, Chapter 1].

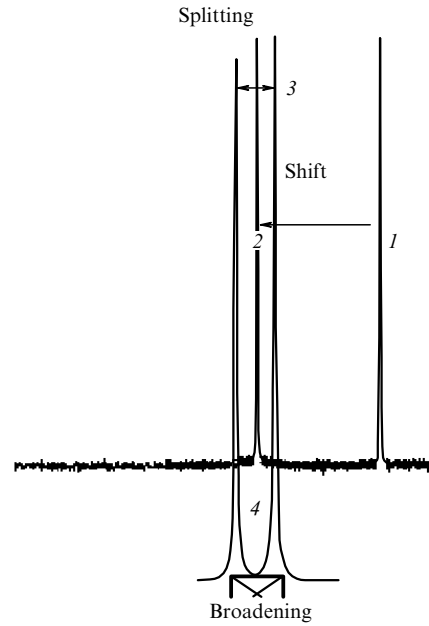


Figure 1. Formation of the magnetic resonance spectrum (schematic): (1) single line of noninteracting equivalent spins; (2) line shift due to interaction with the environment (for example, due to shielding); (3) line splitting (for example, due to interaction with spin 1/2, which has two orientations), and (4) line broadening as a result of the presence of inhomogeneities and time-dependent interactions.

populations of these levels ('polarization') and to the appearance of a macroscopic paramagnetic moment, which is characterized in the limit by the reservoir temperature (Curie's law for paramagnets).

Resonance is observed under irradiation-frequency sweep near the resonance value or using Fourier analysis (equivalent to such a sweep) of the system response to a pulsed switch-on of the resonance frequency. As a result, a line of magnetic resonance is registered (Fig. 1) or a spectrum of magnetic resonance is registered, the latter containing several lines. The relative value of the linewidth $\delta\omega/\omega_0$ in the majority of paramagnetic resonances appears to be uniquely low⁵ (down to 10^{-9}), and the resolution of the paramagnetic resonance spectra to be correspondingly high. This is explained by the weak coupling of spins with the 'lattice'. At the same time, the parameters of the spin Hamiltonian are determined by the spin interactions with the environment (by the so-called spectrum-structural correlations), which makes it possible to distinguish the spin lines in very similar but nevertheless different positions.

Experimenters select the conditions of magnetic resonance by varying the parameters of the polarizing and exciting fields, i.e., the magnetic field strength (induction) and the frequency (or phase) of vibrations, in time. This makes it possible to change the intensity, frequency, and width of lines of spins of the same type in the same object by changing not the object itself, but only the conditions for the excitation of magnetic resonance (using resonances in the rotating coordinate system, the rotation of the sample, double resonances, pulsed methods of line narrowing, etc.). Each spin individually or a certain combination of spins coupled

⁵ This narrowness of the lines partly compensates for the low integral intensity of the signal (the problem of the sensitivity of the magnetic resonance methods will be considered below in this section and in Section 3.7).

via some interaction (spin system or subsystem) serves as a sensor (system of sensors) located in the structure of the substance. The symmetry and the type of spin Hamiltonians are determined by the constitution of the molecules or crystals in whose structure the spins are included. For example, the number of lines or groups of lines is determined by the number of nonequivalent positions of spins. If the spins are identical and if their interaction with the surroundings can be neglected, then only a so-called Zeeman Hamiltonian remains in a field \mathbf{H}_0 :

$$\hat{\mathcal{H}} = -\boldsymbol{\mu}_S \mathbf{H}_0, \quad (1.3)$$

and only one line of magnetic resonance is observed at the resonance frequency $\omega_0 = \gamma H_0$ [chemical and magnetic equivalence of spins with a gyromagnetic ratio γ (see line 1 in Fig. 1)].⁶ The additional ('spectrum-forming') interactions produce the magnetic resonance spectrum. The interaction of spins with the environment (for example, with the electron shells, with the electrical and magnetic fields of the environment) leads to a shift of the resonance frequency (line 2 in Fig. 1). The interaction with other spins can also lead to a line splitting in the spectrum (line 3 in Fig. 1). Some time-dependent interactions determine a relaxation broadening of lines⁷ (see line 4 in Fig. 1). The different lines in the resonance spectrum belong to nonequivalent spins (relating to different particles or located in different environments). The states that 'live' for only a short time and pass into each other give one line in the spectra. The 'switching-on' of chemical exchange or spin relaxation of the spin which interacts with the spin that is being observed can lead to the reverse merging of lines 3 in Fig. 1 into a single line.

The most important role in the theory of macroscopic manifestations of magnetic resonance belongs to the Larmor theorem [8]. According to this theorem, the behavior of a system with a mechanical moment L and magnetic moment M in the field H directed along the z -axis is equivalent to its behavior at $H = 0$ in the coordinate system which revolves uniformly about the z -axis with an angular (Larmor) frequency $\omega_0 = \gamma H$, where $\gamma = M/L$ is the gyromagnetic ratio. As an obvious consequence of the law of conservation

⁶ The resonance frequency $\omega = \gamma B$ (just as the Lorentz force, Biot-Savart law, etc.) in modern textbooks (see, e.g., Ref. [2, Chapter 7, Section 13]) is expressed through the induction B . I E Tamm uses B only in the microscopic Maxwell equations [3, p. 428]. Landau and Lifshitz [4, p. 150] indicate that the average value of the magnetic field strength in the microscopic consideration is usually called the induction B , but in the formulas for these quantities the designation H is usually employed. Generally speaking, in early sources (in articles written by the discoverers of magnetic resonance and some others published before the 1970s and in many cases even later) the expression $\omega = \gamma H$ is used. The confusion in the designations, which became even stronger in the process of introducing the International System of Units (SI) (cf. the use of designations B and H in two monographs devoted to the application of high-resolution NMR in solids [5]), has gone virtually without discussion. It is only pedantic H Kopfermann [1, Preface], with a reference to G Mie [6] and A Sommerfeld [7, Preface], who indicated that in these formulas H is indeed the designation for induction (*sic!*). Following this 'German' or 'magnetic-resonance' tradition, we use the Gaussian system of units and formulas with H . In the Gaussian system of units for a vacuum, the induction B in gauss is identically equal to the strength H in oersteds. For the characteristics of the magnetic fields in spectrometers, we give, as is accepted at present, the values of B in SI units, i.e., in teslas ($1 \text{ T} = 10^4 \text{ G}$).

⁷ The lines are also broadened in inhomogeneous systems (powders, glasses, and crystals with dislocations), where the parameters of the Hamiltonian are different in various parts of the sample.

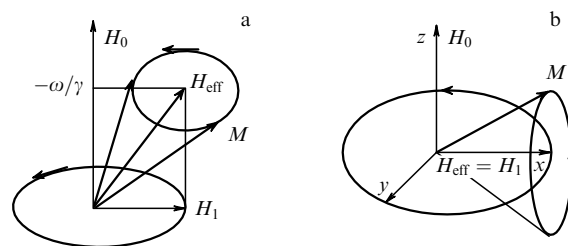


Figure 2. A schematic of the motion of a magnetic moment in a field H_0 according to Larmor theorem [Eqn (1.4) without allowance for relaxation terms]: (a) general case (precession about H_{eff}), and (b) the case of an exact resonance (precession about H_1).

of the moment of momentum, this theorem is also valid in the description of microscopic effects. The passage to a coordinate system rotating about the z -axis is equivalent to the switching-on of a field with frequency $-\omega_0/\gamma$, directed opposite to the field that acts in the laboratory coordinate system (Fig. 2). The essence of the Larmor theorem (the gyromagnetic effect), also with allowance for relaxation effects, is expressed well by the vector equation (Bloch equation [9])

$$\frac{d\mathbf{M}}{dt} = -\gamma[\mathbf{M} \times \mathbf{H}] - \frac{\mathbf{M}_z - \mathbf{M}_0}{T_1} - \frac{\mathbf{M}_\perp}{T_2}, \quad (1.4)$$

where \mathbf{M}_z and \mathbf{M}_\perp are the longitudinal (parallel to the polarizing field) and transverse (lying in the same plane as the rotating component of the alternating magnetic field) components of the vector of nuclear magnetization, respectively, and \mathbf{M}_0 is the thermal equilibrium value of the macroscopic magnetic moment. The parameters T_1 and T_2 are the relaxation times of the longitudinal (spin-lattice) relaxation [i.e., the time of the establishment of the spin temperature (see below) equal to the temperature of the thermal reservoir] and transverse relaxation (time of the destruction of coherence in the spin precession), respectively. Equation (1.4) can more conveniently be written out in the rotating frame of reference (RFR). In the presence of a rotating (with a certain frequency ω) field⁸ with an amplitude H_1 (Fig. 2a), the effective field H_{eff} in an RFR is expressed in the form

$$H_{\text{eff}} = \sqrt{\left(H_0 - \frac{\omega}{\gamma}\right)^2 + H_1^2}. \quad (1.5)$$

In the case of exact resonance ($\omega = \gamma H$), the z component of the field in the rotating frame is equal to zero (Fig. 2b). Consequently, the magnetic moment in the steady state rotates in unison with the resonance field and simultaneously precesses about \mathbf{H}_1 with a frequency γH_1 .

When the resonance field with a frequency ω is switched on for a finite time τ , the magnetic moment is turned through an angle $\alpha = \gamma H_1 \tau$. This means that with a successful choice of

⁸ The harmonically oscillating linearly polarized field, which is used in practice, is the sum of two fields rotating in opposite directions. This leads to a shift of the frequency of the resonance peak (the so-called Bloch-Siegert shift [10] under the action of the field of 'negative frequency' $-\omega$). However, an analogous shift is also characteristic of any line in the spectrum of electromagnetic absorption under excitation by a linearly polarized field.

Table 1. Some interactions of spin systems under natural and standard technical conditions.

No.	Interaction	Examples of objects	Energy, MHz	Quantizing interaction	Comments
1	Interactions of ‘fine structure’ D (joint action of crystal field ΔE and spin-orbit interaction λ such as $D \sim \lambda^2/\Delta E$, etc.)	Cr^{3+} in Al_2O_3	5723.5	$D[3S_z^2 - S(S-1)]$	‘Zero-field EPR’
2	Quadrupole nuclear spin interactions in the crystal field eQq	Spins of ^{127}I nuclei in SbI_4 Transition $\nu_{(1/2 \rightarrow 3/2)}$ Transition $\nu_{(3/2 \rightarrow 5/2)}$	204.5 409.0	$eQq[3I_z^2 - I(I-1)]$	NQR (has been observed for more than 80 stable isotopes with $I > 1/2$)
3	Interactions with effective fields in a ferromagnet, which depend on the anisotropy, magnetic moment, and demagnetizing factor (K_1, M_0, N)	Electron spin resonance in the absence of an external magnetic field (natural ferromagnetic resonance of little ellipsoid)	Up to 10,000	$\gamma \left(\frac{2 K_1 }{M_0} + NM \right)$	The FMR frequency falls within the range $\frac{\gamma}{2\pi} \frac{2 K_1 }{M_0} < \nu < \frac{\gamma}{2\pi}$ $\times \left(\frac{2 K_1 }{M_0} + 4\pi M_0 \right)$
4	Spin-spin interactions	Electron in a hydrogen atom (according to Fermi)	1420	$AIS = A(I_x S_x + I_y S_y + I_z S_z)$	Here, Fermi hyperfine interaction
5	Zeeman interactions with a magnetic field of planets	Free radicals in the field of (a) Earth, and (b) Jupiter	1.4 11.2–39.2	$\frac{\gamma}{2\pi} \mathbf{H}_0 \mathbf{S}$	Magnetic resonance in the field of cosmic bodies
6	Zeeman interactions with a magnetic field of devices (commonly accepted values)	(a) ^1H NMR spectrometer for chemistry, (b) ^1H MR tomograph for clinical medicine	300–600 10	$\frac{\gamma}{2\pi} \mathbf{H}_0 \mathbf{I}$	Magnetic resonance in an artificially induced magnetic field

General note: Conversion from the EPR frequency of free radicals to ^1H NMR frequency in the same field necessitates dividing by 658.5. The cases 5 and 6 are examples of magnetic resonance in ‘strong field’ or ‘standard’ magnetic resonance.

the parameters of the pulse ($\alpha = \pi/2$, a 90° pulse) it is possible ‘to place’ the magnetic moment into the plane perpendicular to the field H_0 and thus attain the maximum value of the amplitude of the signal of ‘free induction’, the signal induced by the freely precessing moment in the receiving coil.

An analysis of the phenomena of magnetic resonance in a rotating frame of reference is important for the theory; this analysis made it possible to propose diverse and efficient procedures for experimenting (the passage from a strong magnetic field to a weak one and vice versa).

Magnetic resonance or, more precisely, magnetic resonances in the condensed media became the basis of methods for studying spin systems. The variety and the unique character of magnetic resonances is determined by the relationships between different energies of spin interactions, namely, with the external field (ω_z), with local fields (ω_{loc}), with unlike spins (ω_{IS}), and between like spins (ω_{SS}) (the energies are given in frequency units). The interaction that considerably exceeds all others in energy serves as quantizing (assigning the eigenstates of a system) and as polarizing (determining the populations of the states and, thus, the value of the total magnetic moment).⁹ The polarization in a thermal equilibrium state is determined by the Boltzmann

relation for the level populations, $\exp[-\omega\hbar S_z/(3kT_L)]$, and in nonequilibrium states the parameter T_L is replaced by the so-called spin (effective) temperature T_S . For magnetic resonances, the case of ‘high’ temperatures ($\omega\hbar \ll kT_L$) is usually the characteristic one.

A schematic picture of the classification of magnetic resonances, based on the type of the main, i.e., quantizing, interaction, is given in Table 1 where we present some types of quantizing interactions that lead to the formation of a system of levels, transitions between which correspond to the diverse variants of magnetic resonance. Among these, EPR in a zero field [11] and nuclear quadrupole resonance (NQR) [12] are excited in the systems with spins $S \geq 1$, and all the other resonances are excited in the systems with any nonzero values of the spin (some cases will be considered below).

When the Zeeman interaction serves as a quantizing interaction, in the first approximation (without taking into account spin–spin and multipole interactions) the magnetic resonance spectrum contains a single line. The allowance for weak interactions between spins leads to spectra that are analogous to those presented in Fig. 1.

A schematic representation of the ranges of magnetic resonance in the case where the Zeeman interaction plays the part of the quantizing interaction is given in Fig. 3 which displays (on a logarithmic scale) the dependences of the magnetic resonance frequencies $\nu = \omega/(2\pi) = \gamma H/(2\pi)$ on the magnetic field induction for three particles with gyromagnetic ratios differing by two–three orders of magnitude, namely, free electron e^- , proton ^1H , and the nucleus of the

⁹ The populations of states whose energy depends on the squares of magnetic quantum numbers m^2 (NQR, EPR in a zero field), rather than on the numbers m themselves, determine spin alignment rather than their polarization.

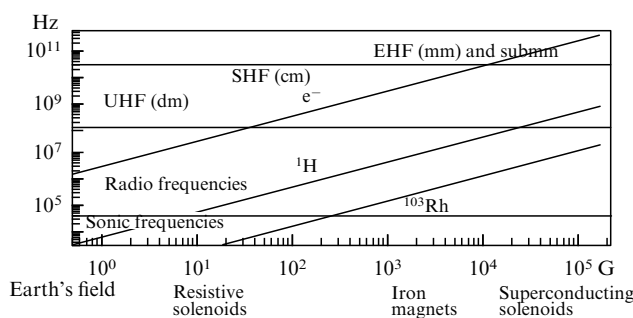


Figure 3. Ranges of paramagnetic resonance in external magnetic fields. Along the abscissa axis, possible sources of such fields are indicated; along the ordinate axis, resonance frequencies and the corresponding ranges of electromagnetic waves are given. All the scales are logarithmic. Three dependences are plotted: for a free electron (e^-), for a proton (^1H), and for the nucleus of a rhodium ^{103}Rh isotope.

rhodium ^{103}Rh isotope (in descending order of the magnitude of γ).¹⁰ The diagram is accompanied by indications of the appropriate ranges of radio frequencies (wavelengths) and the sources of a magnetic field.

In Fig. 4, we display the diagram of frequencies and relative values of the sensitivity of magnetic resonance detectors (see below) at the lines with identical broadenings and identical numbers of spins of a given type in the sample; in particular, points for the ‘free’ electron e^- , proton ^1H , and some nuclides are shown. The wide frequency range in which magnetic resonance can be observed makes for a variety of techniques in the related experiments.

The problem of the sensitivity (signal-to-noise ratio, S/N) of the magnetic resonance methods is of fundamental importance for evaluating the potential of these methods in different applications. We will return to this problem several times again and will consider it in the most detail in Section 3.7, where we will discuss the ultimate sensitivity (detection of the signal from a single spin).¹¹

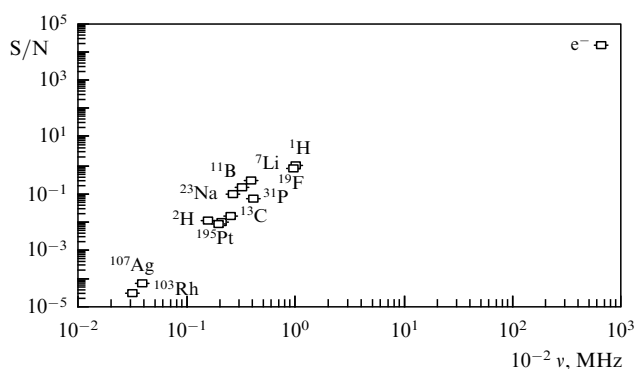


Figure 4. Diagram of the relative frequencies ν and sensitivities (signal-to-noise ratios, S/N) of the magnetic resonance signals from different particles (electron and nuclides) at identical magnetic field strengths (2.35 T) and identical numbers of spins in the sample.

¹⁰ Of great interest is the question of whether or not the magnetic resonance of a neutrino could be obtained, whose magnetic moment is, according to modern estimates, no more than $10^{-19}\mu_B$. At present, a negative response is accepted without question.

¹¹ The values of S/N depend not only on the gyromagnetic ratios, but also on the spin numbers I (see, e.g., the estimations for the induction method

The energies of the quantizing (and, all the more, other) interactions for the overwhelming majority of spin systems are negligible in comparison with the thermal energy at normal temperatures. The Heisenberg exchange interaction between electron spins, whose energy is characterized by the Curie temperature T_C (or Néel temperature) which reaches $10^1 - 10^3$ K, does not explicitly influence the frequency of magnetic resonance for ferromagnets and antiferromagnets. For applications, there are also important ‘spectrum-forming’ interactions determining both the spectra of magnetic resonances and the contours of spectral lines, and also interactions that determine the rates of relaxation of the spin system and the establishment of its equilibrium with other degrees of freedom of the substance; in more detail, we will consider this issue in Section 2 (as to the problem of magnetic relaxation, see Ref. [15] for more details). Here, we will only point out that the ‘spectrum-forming’ and relaxation-governing interactions can be separated into a group of interactions that possess a trace (spur) equal to zero, such as the dipole-dipole (DDI), electrical quadrupole (EQI), and spin-rotational (SRI) interactions, and a group of interactions which have a nonzero spur. The last comprise, for example, the shielding of the nuclear spin by electron shells or the chemical shift (CS) in NMR, and scalar interactions between the spins [hyperfine interaction (HFI) between the electron and nuclear spins and indirect spin-spin interaction (ISSI)].

The interactions of the first type engender the spectral picture in rigid systems (DDI and EQI in solids). The spin-rotational interactions become quantizing in isolated molecules in rarefied gases [rotational radiospectroscopy (see, e.g., Ref. [16]). In systems with mobile carriers of spin, such interactions ensure the mechanisms of spin-lattice relaxation. Interactions of the second type cause both relaxation and shifts and line splitting in mobile systems (in solids with mobile molecules, liquids, and gases).

Studies of systems which contain several types of spins are conducted using the simultaneous excitation of resonances at different frequencies, i.e., double and multiple resonances. These are the so-called electron-nucleus, nucleus-electron, electron-electron, and nucleus-nucleus double (magnetic and quadrupole magnetic) resonances. The double optical-magnetic resonances (DOMRs) discovered by Kastler [17] linked the optical effects discovered by Zeeman [18] with the paramagnetic proper (including nuclear) resonance.

In the above designations of double resonances, first and foremost is a resonance that is recorded by the control field and, secondly, a resonance that is usually excited by a stronger field [11, 19]. Among the applications of double resonances, there are methods of pumping and dynamic nuclear polarization (DNP) [20, 21].

Magnetic resonances opened before modern physics and adjacent fields of natural science the possibility of studying a great variety of objects through the research of the structure and dynamics of spin systems.

in Refs [13, Chapter 3, Section 11] and [14]). Therefore, the values for the isotopes of lithium, boron, and sodium with $I = 3/2$ fall out from the linear (on a logarithmic scale) dependence on ν for spins $1/2$. The line broadening was neglected (accepted to be identical). Furthermore, S/N dramatically depends on the methods and equipment used for the observation of the magnetic resonance, of which the basic ones are the induction method, the SQUID method, and the method of mechanical detection (for a comparison of these methods, see Section 3.7).

2. Prehistory, discovery, and studies of magnetic resonances

2.1 Early ('pre-spin' and 'pre-nuclear') prehistory

In 1996, the community of researchers of magnetic resonance celebrated the centenary of Larmor's theorem. The publication of this theorem [8] can be considered the beginning of the prehistory of magnetic resonance. Joseph Larmor (1857–1942) examined a system of particles possessing electric charges and masses and rotating with a constant velocity in a magnetic field. The system has both an angular momentum \mathbf{L} and, as a ring with electric current, a magnetic dipole moment \mathbf{M} (see Fig. 2).¹² The gyromagnetic ratio $\gamma = M/L$ for electrons with a charge e and mass m_e in the Gaussian system of units is expressed, according to Larmor, in the form

$$\gamma_e^L = \frac{e}{2m_e c}. \quad (2.1)$$

The motion of such a gyromagnetic system, as examined by Larmor, in a magnetic field represents a precession of the axis of rotation (axis of dipole) about the direction of the magnetic field \mathbf{H} with an angular (Larmor) frequency $\omega_0 = \gamma H$ (Fig. 2a). Formula (2.1) is valid for the orbital moment of an electron. The concept of the precession of the magnetic moment, which is rigidly connected with the angular momentum, was extended to the spin (intrinsic angular momentum) of the electron, which was discovered 30 years later. The values of the gyromagnetic ratio and Larmor frequency for electron spin proved to be twice as large:

$$\gamma_e^S = \frac{e}{mc} \quad (2.2)$$

(superscripts L and S in formulas (2.1) and (2.2) stand for the orbital and spin angular momenta, respectively).

Both in serious publications and in laboratory jargon, the terms 'Larmor frequency' and 'Larmor precession' are quite usual.

Somewhat earlier, in 1895, the results of the first systematic studies of paramagnets performed by Pierre Curie were published. These results entered into the theory of magnetism and magnetic resonance with the name the Curie (Curie–Weiss) law, which says that the magnetic moment of a paramagnetic sample is inversely proportional to the absolute temperature and linearly depends on the external polarizing field.¹³

The decisive influence on the future discovery of magnetic resonance was exerted by the discovery of the Zeeman effect (splitting of the optical spectrum lines in a magnetic field). Pieter Zeeman (1865–1943) at Leiden University (the Netherlands) in 1896 observed the splitting of spectral lines of the doublet $D_{1,2}$ in sodium vapors [18]. In 1897, this splitting was interpreted by Hendrik Lorentz (1853–1928). A detailed description of the classical Lorentz model of the action of an external magnetic field on electron currents can be found in the well-known textbook of G S Landsberg [22, pp. 512–519].

¹² The Larmor model thus has something in common with the Ampère hypothesis (1820) for 'molecular-ring' currents.

¹³ The Curie–Weiss law is valid only at sufficiently high temperatures; for the case of arbitrary temperatures, it was formulated somewhat later by P Langevin, and for the quantum case, by P Debye and L Brillouin. A Kastler [23, pp. 9–15] considers the contribution made by these authors to be fundamentally important in the prehistory of magnetic resonance.

The studies of the Zeeman effect performed in the first decades of the 20th century were an important contribution to the basis of quantum theory and the theory of spin. In the general case, the orbital and spin angular momenta of an electron in an atom interact with each other and with the external magnetic field (anomalous, or complex, Zeeman effect). The 'simple' Zeeman effect proved to be completely due to spin. The Larmor–Zeeman–Lorentz model confirmed the dependence of magnetic effects in spectra on the field strength and on the parameter $e/(m_e c)$. The interaction of spin with an external magnetic field was called the Zeeman interaction.

It can be said that the Ampérian 'molecular-ring currents' were incarnated in the Bohr electron orbits of atoms. In 1920, Wolfgang Pauli introduced the concept of a Bohr magneton [24, Chapter 3, Section 3]. The value of the elementary magnetic moment (for an electron in the lower orbit of a hydrogen atom) is equal to

$$\mu_B = \gamma_e \hbar = 9 \times 10^{-20} \text{ erg G}^{-1}, \quad (2.3)$$

where γ_e is given by formula (2.1). The concept of the magneton was subsequently extended to the magnetic moments of nucleons and nuclei. The so-called nuclear magneton is defined as

$$\mu_n = \frac{e\hbar}{2m_p c}, \quad (2.4)$$

where the proton mass $m_p \approx 1836 m_e$. The magnetic moment of a proton is equal to approximately $2.67 \mu_n$, while the magnetic moment of a neutron also differs from zero (which, of course, disagrees with the classical Larmor model) and equals approximately to $-1.91 \mu_n$. These values were repeatedly refined by the magnetic resonance methods.

An important contribution to the formation of the theoretical arsenal of magnetic resonance came from the works performed by the German physicist Alfred Landé (1888–1975) in 1919–1921 (see Ref. [25]), and his later work [26]. In these works, the concept of magnetic moments of different nature interacting between themselves was introduced. In the case of a weak coupling between the moments (in strong fields), the magnetic moments of each type interact with the magnetic field independently. In the strongly coupled system of moments (in a weak field), there is a single effective magnetic moment characterized by a single g factor (formulas for calculating it were given in papers [25]).

For an electron, the expression for γ can be written, by introducing the g factor via formula (2.2), in the following form

$$\gamma = g \frac{e}{2m_e c} = g \frac{\mu_B}{\hbar}, \quad (2.5)$$

and the expression for the Larmor frequency as

$$\omega = \frac{g\mu_B H}{\hbar}. \quad (2.6)$$

The Larmor frequency in the literature on EPR is usually written out through the g factor, and in the literature on NMR through the gyromagnetic ratio. For the orbital momentum of an electron, one finds $g = 1$. For the electron spin in the case of a weak spin–orbit coupling, one has $g \approx 2$.

In 1922, a key result was obtained in experimental studies of magnetic quantum effects. The German physicists O Stern (1888–1969) and W Gerlach (1889–1979) attained a spatial separation of an atomic beam (in the first experiment it was a

beam of silver atoms) in a magnetic field into two beams with different orientations of magnetic moments [27]. This work betokened the discovery of electron spin equal to $S = 1/2$ and, if we glance still further forward, it also betokened the possibility of obtaining a system with a negative temperature via a spatial selection of states with a higher energy (subsequently, this was realized in a hydrogen oscillator by N Ramsey and colleagues in 1960). But this work [27], most of all, suggested the possibility of magnetic resonance, since it demonstrated the existence of states which differ only in the orientations of the magnetic moment. This possibility was immediately noted by A Einstein and P Ehrenfest [28]. If there are two states with different energies, this means that there occur quantum transitions between them, spontaneous and induced, since “the Larmor precession characteristic of the classical model is not accompanied by a change in the energy of moments in the magnetic field” [28].

Note that the investigations of gyromagnetic effects in ferromagnets (Einstein, W J de Haas) and of the dispersion of electromagnetic waves in ferromagnets (V K Arkad'ev, R Loyarte) were conducted prior to the beginning of the searches for magnetic resonance and practically independent of these searches.¹⁴ The work by Landau and Lifshitz [29], in which the macroscopic effect of ferromagnetic resonance can be perceived in the conclusions, was also performed prior to the discovery of magnetic resonance, although considerably later.

From 1920 to 1925, the idea of spin was ‘ripening’ gradually. A Sommerfeld and others intensely studied the spectra of excited atoms, including those obtained in a magnetic field. A Compton suggested the possibility of the existence of an intrinsic magnetic moment of an electron, based on the data of experiments on X-ray scattering, which indicated that no rearrangement of electron orbits occurs during the magnetization of a ferromagnetic crystal. Not without the influence of the works of W Pauli, R Kronig and others (see Ref. [24, Chapter 3, Section 4]), it is S Goudsmit (1902–1979) and G Uhlenbeck (1900–1988) who became the authors of the idea of a ‘spinning electron’ with a magnetic moment equal to the Bohr magneton and with a g factor equal to 2 (see Refs [32, 33]). Remember that the hypothesis for the existence of spins in atomic nuclei was advanced in connection with the hyperfine structure of optical spectra by Pauli as early as 1924 [34].

The nonrelativistic theory of spin was developed by Pauli; the Dirac theory substantiated the inevitability of the existence of spin in a relativistic electron. Enrico Fermi, using Dirac's equations, created a theory of scalar magnetic HFIs of spins (magnetic moments) of electrons, S , and nuclei, I , and calculated the magnitude of the HFI for the ground state of an electron in the hydrogen atom (see Refs [24, 35]). This interaction in the literature is frequently called the Fermi interaction *ASI* (or scalar, or contact). Soon, the concept of spin came to occupy the most important place in the physics of the microcosm and condensed state.

¹⁴ An exception is the attempt by Ya G Dorfman [30] [which was initiated by the conjecture made in paper [28] and was by no means convincing (in view of the absence of the theory of spin and of the theory of quantum transitions)] to combine the description of the results of Stern–Gerlach and Arkad'ev–Loyarte into a common quantum paradigm. An analysis of the experimental work on the magnetomechanical effect of Einstein and W J de Haas (anticipated by O Richardson, as well as by S Barnett), which is important for the development of the idea of spin, is given by V Ya Frenkel' and B E Yavelov in Ref. [31, Chapter 4].

2.2 In pursuit of nuclear magnetic moments

The order of magnitude of the proton magnetic moment at the beginning of the 1930s had already been known from low-temperature experiments on the heat capacity of hydrogen, but the precise values of the magnetic moments of other nuclei remained only to be guessed at. Otto Stern, together with Immanuel Esterman (1900–1973) and Otto Frisch (1904–1979), in 1933 published the results of experiments with molecular beams (isotopomers of hydrogen: H_2 , HD, D_2) in a vacuum and with the sorting of these particles according to their energies of interaction with the magnetic field [36, 37] analogous to the experiments with atomic beams [27].¹⁵ Experiments with the molecular beams of particles whose magnetic moment is wholly caused by nuclear paramagnetism have also been carried out since 1934 at Columbia University (United States) under the guidance of Isidor Rabi (1898–1988). The theorists Fermi, E Segres, A Landé, and also I E Tamm and S A Al'tshuler in 1933–1935 discussed the theory of the formation of nuclear magnetic moments.

In 1936, Khar'kov physicists from the Ukrainian Physico-technical Institute (UFTI) B G Lazarev (1906–2001) and L V Shubnikov (1901–1938) measured the contribution of protons to the magnetization of solid hydrogen [38].

C J Gorter (1907–1980) was the first to attempt, albeit unsuccessfully, to observe NMR in solids (in potassium alum and lithium chloride, using the thermal effect of resonance absorption) [39].

Rabi's laboratory became the first in the world to fix the radiofrequency-field-excited transition between states in spatially separated beams [40]. In Rabi's experiments, the resonance was for the first time obtained in the 7Li nuclei. Then, there followed other observations of resonance in the 7Li , 6Li , ^{39}K , and ^{35}Cl nuclei. In the same laboratory, the magnetic resonance methods were applied to refine the values of the magnetic moments of 1H and 2H , the magnitudes of the electrical quadrupole nuclear moment of deuterium, and the values of the Zeeman interactions and scalar (hyperfine) interactions of an unpaired electron in alkali metal atoms with their nuclei [41]. In the last work, the electron paramagnetic resonance with its hyperfine structure caused by interactions with nuclear spins in different orientations was for the first time observed in atomic beams.

It is paradoxical that, after the failure with NMR [39], C J Gorter and colleagues did not attempt to observe EPR. They measured the dependence of the alternating magnetic field energy absorption by paramagnetic materials on the strength of a constant magnetic field in fields that were too strong (and at frequencies that were too low) for the observation of EPR. In 1942, Gorter and L Broer again carried out searches for NMR using a sensitive radiophysical method of detecting resonance absorption [42]. This was the generator response method, one of the versions of which E K Zavoiskii called the ‘grid current’ method. And again the Dutch physicists failed because of an improper selection of the object and inappropriate observation conditions. They investigated crystals (LiCl and KF) practically free of paramagnetic impurities and, furthermore, following the paradigm of the Leiden school, at low (liquid-helium) temperatures. However, the samples which they selected for study were characterized by extremely long relaxation times.

¹⁵ The Nobel Committee for Physics decided (see Appendix) that it is precisely O Stern and his colleagues who deserve the honor of the discovery of the proton magnetic moment.

NMR relaxation would be more effective in electronic paramagnets and at higher temperatures, whereas in diamagnetic compounds, and at ultralow temperatures at that, the resonance field results in a leveling off of the populations of spin states, which is equivalent to the demagnetization of the system (saturation effect).

The answer to the question of why Gorter did not attempt to reveal EPR obviously lies in the fact that the EPR lines were expected to be too wide, as was noted in a report at an international conference in 1969 [23, pp. 15–25]. Gorter, however, just like other researchers, did not know that at a sufficiently large concentration of spins in a substance an effect of exchange contraction of the resonance line can show itself. This effect (exchange-interaction-induced narrowing) was examined by Gorter and van Vleck [43] already after the discovery of EPR. Van Vleck [44] showed that the exchange interaction does not change the second moment of the spectral line contour, but decreases its fourth moment, i.e., the observed line becomes narrower. The conditions under which the observation of EPR at a frequency on the order of ω_{EPR} becomes impossible because of line broadening can be written out as the following inequality

$$\delta\omega \geq \omega_{\text{EPR}} \approx \gamma_e H \quad (2.7)$$

where $\delta\omega$ is the linewidth, which for the samples investigated by Gorter will change to reverse one if we simultaneously increase H and ω approximately threefold, or if we simply take a sample with a narrower line (as Zavoiskii did it).

Note that at the beginning of the 1940s, besides the above-mentioned work on paramagnetic relaxation and the observation of EPR in atomic beams, most important works which soon became the foundation of the theory of EPR of transition-element compounds have already been performed. This is the work of H Bethe, H Kramers, and J van Vleck, and other work on the theory of the effect of surroundings ('crystal field') on paramagnetic ions (for references, see, e.g., the monograph [11]—the 'bible' of EPR), the most important work by van Vleck about paramagnetic relaxation [45], etc.

The pursuit of the resonance of nuclear magnetic moments in a substance was interrupted by the World War II. But the discovery of EPR in condensed media occurred before the end of the war.

2.3 Discovery of electron paramagnetic resonance

The circumstances of the EPR discovery made under the severe conditions in Kazan' by E K Zavoiskii during wartime place this event out of the customary series of achievements of physics in the 20th century. This occurred "in years of ordeal, times of woe"¹⁶, when everything aligned against the researcher. But let us begin at the very beginning.

Under the most difficult conditions of the weakened Physics Department at Kazan' State University (KGU in *Russ. abbr.*) (see Ref. [46, pp. 212–222]), Zavoiskii became an experienced radio technician and radio physicist and then a teacher and organizer of research work. In the beginning of 1940, there arose a 'triple alliance' at the KGU Physics Department, which consisted of a skillful experimental physicist Evgenii Konstantinovich Zavoiskii, a talented and excellently qualified theorist Semen Aleksandrovich Al'tshuler, and an experienced physical chemist Boris Mikhailovich

Kozyrev. Their main target was NMR. Zavoiskii was searching for nuclear magnetic resonance, but discovered electron paramagnetic resonance ('Columbus's casus,' a very frequent event in the history of scientific discoveries!).

Zavoiskii systematically carried out experiments on the detection of magnetic resonances (see Ref. [46, pp. 12–17]). Until May 1941, there seemed to be no hope for a positive result. But precisely at that time signals began appearing (apparently, caused by the NMR of protons). The setup was restored through the efforts of I I Silkin, the keeper of the museum–laboratory of E K Zavoiskii in KGU, and described in Ref. [46, pp. 114–118] (see also Ref. [47]), made it possible to sporadically observe NMR signals. An obstacle on the path to the reproducible observation of NMR was the inhomogeneity (variations) of the field, $H_0 \pm \delta H$, in the volume of the specimen, which led to a broadening of the resonance line to values on the order of $\delta\nu = \gamma\delta H/(2\pi)$. The displacements of the ampoule with the specimen and the switching off and on of the magnet led to changes in δH which proved to be practically unpredictable (the dimensions of the specimen were of the same order as the dimensions of the magnet gap). A different magnet was required. But—the movement toward discovery was stopped. Here is an excerpt from Zavoiskii's notes [46, p. 224] concerning the circumstances of the arrival of a special commission at KGU, which had to estimate the research themes in connection with the move of certain institutes of the USSR Academy of Sciences to Kazan' after the beginning of the war. This excerpt here and there resembles the stage directions of a dramatist for a silent scene for a disjointed tragedy:

"Members of the Commission entered Laboratory No. 5 without knocking. At this moment I was observing nuclear magnetic resonance, sitting at the installation and changing the current in a Dubois electromagnet with the help of a rheostat... The members of the Commission crossed the beam of light passing from the galvanometer to the scale and stopped, paying no attention to my gesticulations. They waited for half a minute, and then the phrase was heard: 'Everything here is homemade and is not of any scientific value.' (Evidently, I myself also fell into this category) I wanted to speak, but the Commission had already started towards the door. Everything was over. I was told: 'If you do not get everything out of the room tomorrow, we shall post a sentry at the door with an order not to let you in.' I could not demolish the installation... But the threat was executed, the room was looted, the equipment was thrown out like rubbish, and for one and a half years in room No. 5 bread was distributed for the stuff of the Ioffe Institute." (Translated by Kochelaev and Yablokov). [See also Kochelaev B I, Yablokov Yu V *The Beginning of Paramagnetic Resonance* (London: World Scientific, 1995).]

By this time, S A Al'tshuler had left for the front, and B M Kozyrev had quit KGU. Zavoiskii was forced to participate in the unsuccessful work on the secret 'device No. 1'. In 1942–1944, Evgenii Konstantinovich was repeatedly directed toward practical work. He carried out tasks for the defense enterprises of Kazan', and starting in 1943 he renewed giving the course of general physics. But already in 1943, Zavoiskii returned to the search for magnetic resonance. The Chairman of the Department of Theoretical Physics Ya I Frenkel' granted Zavoiskii a room on the second floor of the Faculty of Physics and Mathematics of KGU (now, the museum honoring E K Zavoiskii is established there).

¹⁶ From Boris Pasternak (Translated by Christopher Barnes).

It is evident from E K Zavoiskii's laboratory notes [47] that he intended to study paramagnetic relaxation in as broad a range of conditions as possible for quite different samples, among which there were crystalline salts of 3d transition metals, such as $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{CuCl}_2 \times (2 + n)\text{H}_2\text{O}$, $\text{MnSO}_4 \times 5\text{H}_2\text{O}$, and their aqueous solutions, as well as some ferromagnets (finely dispersed nickel and iron). The replacement of the permanent magnet in the setup by Helmholtz coils enlarged the search range toward lower frequencies (to $10^7 - 10^8$ Hz).

The change in the experimental conditions automatically put Zavoiskii on a path that facilitated the observation of EPR, which at the same frequency must be observed for a free electron in a magnetic field whose strength is approximately 658.5 times lower than the strength of this field in the case of the proton magnetic resonance. Some samples possessed relatively narrow EPR lines (see the above remark on the exchange narrowing [23, pp. 15–25; 44]). In the curves of the dependence of the grid current on the magnetic field strength at a constant frequency of irradiation, peaks were observed in the region supposedly corresponding to EPR, and a change in the frequency led to the expected shift in the signal. Zavoiskii obtained moral support from Ya I Frenkel¹⁷ and in July 1944 he presented to the Physical Institute of the USSR Academy of Sciences (FIAN in *Russ. abbr.*) a doctoral dissertation on the "Paramagnetic absorption in perpendicular and parallel fields for salts, solutions, and metals". The interpretation of sufficiently wide absorption peaks in the perpendicular fields as being due to spin resonance caused a stir among FIAN experts. The dissertation was not considered for several months. This impelled Zavoiskii to turn to another authoritative center—the Institute for Physical Problems (IPP).

Under the sponsorship of P L Kapitza, A I Shal'nikov (1905–1986) volunteered to help Zavoiskii. In two weeks, they constructed two setups. First, they reproduced Zavoiskii's first Kazan' experiments [49, 50] at a frequency on the order of 10^2 MHz. Then, in a considerably stronger magnetic field (using an imported klystron for the generation of electromagnetic waves with a frequency of about 1000 MHz), the same resonance effects were observed even more distinctly. And, finally, in some samples the experiments were reproduced at liquid-hydrogen and liquid-helium temperatures (see Refs [51, 52]).

So, the mutual aid of Soviet physicists made it possible to bring the first stage of work on discovering and investigating the electron paramagnetic resonance effect to logical completion. On January 30, 1945, Zavoiskii successfully defended his dissertation (see excerpts of the shorthand record in Refs [47, pp. 153–157] and [53]).

2.4 Nuclear magnetic resonance is next on the agenda, again

Only a half a year passed after the friendly critical remarks and modest accolades sounded at the defense of Zavoiskii's doctoral dissertation at FIAN. In the United States, in two laboratories physicists renewed the search for nuclear magnetic resonance in condensed media. After the interrup-

tion for the participation in defense projects¹⁸ during the WWII, American physicists returned to excellently equipped laboratories where they had a wide choice of devices and great opportunities for collaboration with associates. Remembering the small Dubois magnet with a gap diameter of only a few centimeters in the installation constructed by Zavoiskii, we note here that E Purcell, H Torrey, and R Pound (physicists at MIT) used a magnet with a uniform field that had been earlier employed for studies of charged particles in cosmic rays, and F Bloch and co-authors utilized the magnet from a cyclotron [54, Vol. 1, pp. 1–158]. As the sample for observing the proton magnetic resonance in Purcell's laboratory, they used approximately 1 kg (with a volume on the order of 1 dm^3) of paraffin ($(\text{CH}_2)_n$). They placed the sample into a resonator that was included in a balanced (bridge) radio-frequency circuit and waited until a disturbance of the balance appeared due to the excitation of magnetic resonance because of a change in the radio-frequency complex susceptibility of nuclear moments under resonance conditions. On the advice of I Rabi, the experimenters maintained the sample in the magnet for a whole night, in order 'to magnetize' the protons of the paraffin (it was expected that the relaxation time reached several hours, if not to a few days; in reality, it proved to be several minutes). At first, no signal appeared, as it turned out, because of an error in the magnet calibration. But when they established the current at the maximum value and began decreasing it gradually, the measuring device pointer shuddered... This was the first reliable observation of NMR in a solid in the world [55].

At Stanford, Bloch implemented, with the aid of his associates, the idea of so-called nuclear induction, which (in our opinion) was directly prompted by the Larmor theorem and by the Faraday equation of electromagnetic induction.

In a magnetic field directed along the z-axis, let one coil, with the axis along the x-axis, act on the nuclear moment and excite the precession of the magnetic moment. Then, in another coil, with the axis oriented along the y-axis that is perpendicular to the axis of the first coil, the precessing nuclear magnetic moment, in turn, induces a voltage which can be fixed by minimizing the amplitude and adjusting the phase for the direct pick-up from one coil to another. For the investigation, they selected water and aqueous solutions of paramagnetic salts (catalysts of relaxation, as they were called in the laboratory jargon).

The outstanding theorist F Bloch not only suggested the idea of the experiment [Bloch (crossed) coils], but also developed [56] the most known modification of the dynamic equations of the macroscopic magnetic moment, the so-called Bloch equations (1.4). The discovery of NMR completed the basic stage of the evolution of the ideas and methods of magnetic resonance. This evolution—from the Ampérian ('molecular-ring') currents, through the theory of static magnetization, Larmor, Zeeman, and Stern effects, and the establishment of principles of the theory of spin systems to the experiments on resonance in continuous media (see below)—is presented schematically in Fig. 5.

¹⁷ Frenkel' published a formal theory of the broadening of paramagnetic resonance lines in 1945 [48]; however, the absence of a comparison between the results of calculations and experimental data, as well as the absence of a consideration of the mechanisms of dissipation and of any other meaningful conclusions, lessened the value of this work.

¹⁸ According to Ref. [54], one of the authors of the NMR discovery, F Bloch, had been working for a while in Los Alamos, but then joined the Radiolocation Research Laboratory (RRL) at Harvard, where his associate U Hansen worked at that time. E Purcell and his co-authors H Torrey and R Pound worked at the Massachusetts Institute of Technology (MIT) and remained there after the war. Bloch and Hansen returned to Stanford (California) in September 1945, where M Packard joined them.

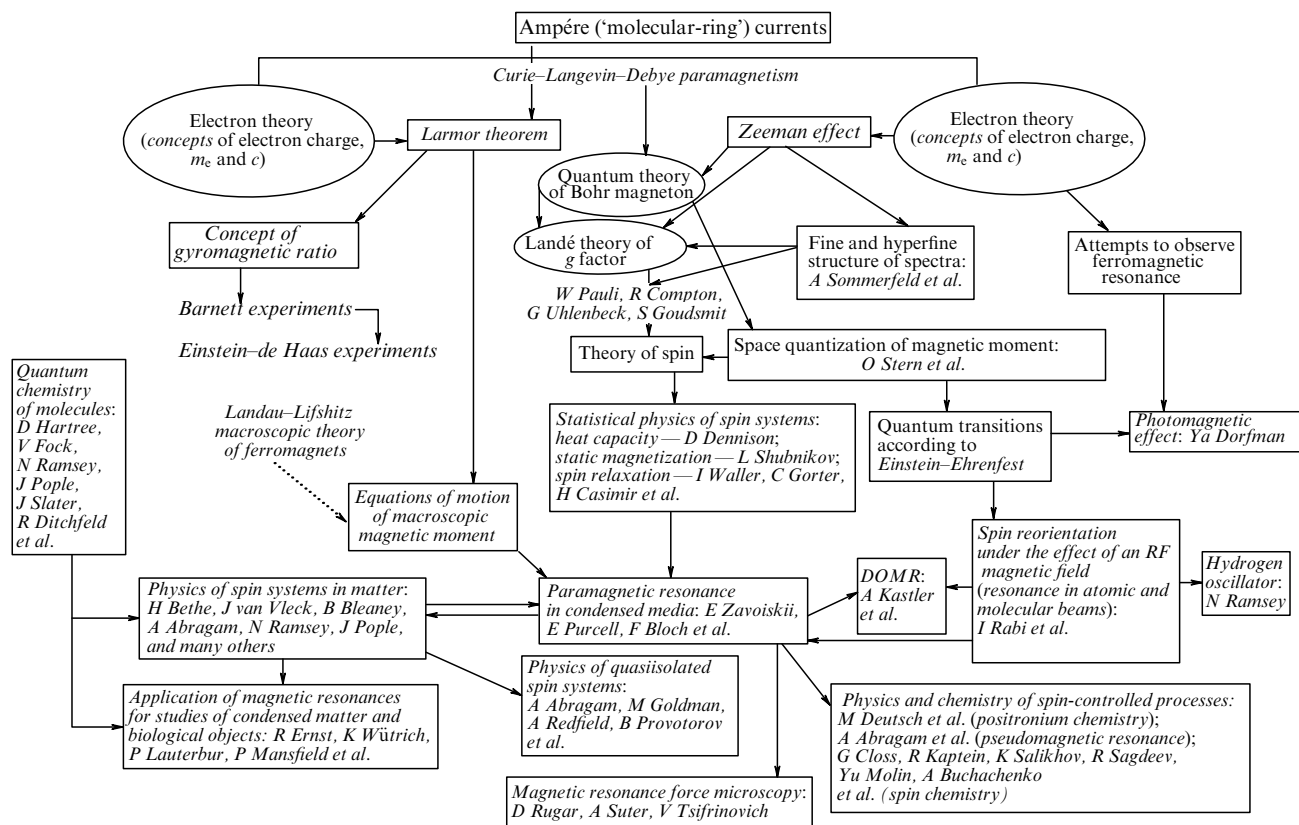


Figure 5. Schematic of consistent evolution of ideas, methods, and applications of magnetic resonance.

2.5 The first years of magnetic resonance

The name Zavoiskii was mentioned at one of the first international conferences on radiospectroscopy (A Kastler, C Gorter, and B Bleaney [57, pp. 169–204]), but Zavoiskii himself was working at that time (as a backroom boy) on the Soviet A-bomb project. The work of those who continued in this field, S A Al'tshuler and B M Kozyrev, was unjustifiably classified. The academic trip of Academician A A Andronov, A M Prokhorov, and K V Vladimirkii to a conference in Amsterdam (1950) was prohibited by the Soviet Government (see Ref. [58]), although Soviet scientists in 1950 had much to say at this conference (see, e.g., Refs [59–62]). The appearance of E K Zavoiskii, who had published 18 works on EPR by then, would have allowed the Nobel Committee to consider his candidacy as equal to those of Purcell and Bloch for the nomination for the Nobel Prize for the discovery of paramagnetic resonance in condensed media. But, as is known, this did not happen.

The development of research into magnetic resonances gradually took the path of studying interactions of spins between themselves and with the substance. For five years after the discovery of NMR, the effect was observed for 83 isotopes of many elements of the Periodic Table [63]. In these years, Bloch's team and the group of Bloembergen, Purcell, and Pound (BPP) (see, e.g., Ref. [64]) established the basic laws governing relaxation processes in liquids. In 1947, the first (in the Soviet Union) report on the observation of NMR was published by K V Vladimirkii [60]. There were discovered (W C Dickinson, W G Proctor, J Zimmerman, H S Gutowsky, C P Slichter, E R Andrew et al.) shielding effects of nuclear moments by electron shells and the related

effects of chemical shift (CS) and the scalar indirect spin–spin interactions (ISSI) caused by the mutual polarization of nuclear spins of different atoms in one and the same molecule through common molecular orbitals (see references cited in the early monographs [63, 65], our survey [66], and the Internet site of S Sýkora [67]).

The NMR method attracted the serious attention of chemists, and on the initiative of J Shoolery, P Arnold et al., the US firm Varian (Palo Alto, Ca.), which was named in honor of Russell and Sigurd Varians, two of the founders of the firm and inventors of a klystron, began the production of commercial NMR spectrometers. The quantum-chemical theories of CS and ISSI, which were initiated by N Ramsey and continued in studies by J Pople, F Santry et al. (see below, and also the references cited in Refs [66, 67]), triggered the development of a number of new very effective avenues in the theory of the structure of molecules, which made it possible to reliably interpret NMR spectra at present.

Investigations in the field of EPR were widely developed (see, e.g., Refs [57, 68–74]) by that time. Apart from the studies in this field performed by Zavoiskii himself, the first works by foreign scientists devoted to studying EPR in compounds of 3d, 4f, and other series of transition elements of the Periodic System appeared. Among these, there were the first works in the West on EPR due to R L Cumberow and D Halliday (USA) [69] and numerous works by British researchers from Oxford, e.g., D M S Buggley et al. [68], A Abragam, M Pryce [70].

The work by Bleaney, Pryce, and Abragam laid the foundation for the approach of an effective spin with an anisotropic g factor and 'fine' splitting [11, Chapter 7,

Section 15, pp. 21–27].¹⁹ The spin of an electron that occupies an orbit with a nonzero orbital moment in transition-metal ions suffers a noticeable spin–orbit interaction and, generally speaking, forms a unified energy system with the orbitals of the d- and f-electron shells of the paramagnetic ion. The spacings ΔE between the magnetic sublevels of such a system of paramagnetic compounds of transition elements can both be comparable in magnitude to a thermal energy $k_B T$ and differ strongly from $k_B T$ in magnitude (to be much greater or much less). For $\Delta E \ll k_B T$, the effective spin is equal to the total spin of the electronic state of the molecule investigated. In the opposite case, high-lying energy levels with an energy $\Delta E \gg k_B T$ under experimental conditions prove to be unpopulated and affect only slightly the behavior of the electron system in the magnetic field.

Thus, if the number of magnetic sublevels that lie in a range of order $k_B T$ is equal to N , then the effective spin of the system at temperatures on the order of T is defined by the relationship $S_{\text{eff}} = (N - 1)/2$, where these N states are transformed one into another upon the symmetry operations corresponding to the crystal lattice in which the ion is located.

The concept of the effective spin also proved to be applicable to so-called non-Kramers ions, for example, Ni^{2+} , whose lower level is spin-nondegenerate [11, Chapter 1, Section 4]. For one and the same ion in different environments, there are possible systems with different effective spins, for example, $S = 0$ and $S \neq 0$ (again Ni^{2+}). In the spin Hamiltonians for spins that are greater than $1/2$, along with the Zeeman interactions, those that depend on the even degrees of magnetic quantum numbers are taken into account. In the presence of a strong external magnetic field, they serve as ‘spectrum-forming’. For $S \geq 1$, in the electron spin Hamiltonian there appear quadrupole and other terms, which depend on the highest degrees of the spin projections $\hat{S}_{x,y,z}^{2n}$ [11, 71].²⁰

EPR, which was discovered in compounds of transition metals, was soon discovered in paramagnetic systems of a different nature. In 1949, EPR was observed for the first time in crystals with radiation damage [72], and from 1947 to 1950, in molecules with unsaturated valences (free radicals) [62, 73, 74]. In Ref. [74], the authors observed the resonance in crystals of a stable free radical of diphenylpicryl hydrazil (DPPH), whose EPR signal, because of the exchange contraction, is so narrow that DPPH became a standard for tuning EPR spectra.

¹⁹ The adjective ‘fine’ is justified when comparing this splitting with the frequencies in optical spectra. But in EPR spectra these splittings are frequently only a little less (a few hundred MHz for Mn^{2+}) and sometimes even comparable (in fields of about 0.3 T and at EPR frequencies on the order of 10 GHz for Cr^{3+} in Al_2O_3) and often even much greater than the EPR frequencies in technically achievable magnetic fields (several hundred GHz and a few THz for many paramagnetic ions). Just like the shifts in the g factors, this effect is due to a combination of effects of the crystalline field (splitting of orbital levels) and spin–orbit coupling. These interactions are determined by the symmetry of the surroundings of the paramagnetic ion, its electronic state, and the relationship between the energy of spin–orbit interaction and the energy of splitting of the ion levels in the crystal field [11].

²⁰ Among the first monographs devoted to the theory of the EPR spin Hamiltonian, there was one by the Soviet physicists S A Al'tshuler and B M Kozyrev, *Electron Paramagnetic Resonance* (1961) [71]. Already in the first edition, it contained a vast bibliography; in the second edition, the number of references reached a record number of 2499 (see also comments in Ref. [66]).

In the late 1940s and more recently, the methods of magnetic resonance in ordered magnetic phases [antiferromagnetic and ferromagnetic resonances (AFMR and FMR, respectively)] became widely developed. Here, a resonance of the macroscopic (classical) magnetic moment of an ensemble of electron spins occurs, rather than the magnetic moments of separate atoms, as in the case of paramagnetic materials (see Refs [75, 76]). In 1946–1947, J H E Griffiths and E K Zavoiskii discovered, independently of one another, FMR [77, 78].²¹ NMR in ferromagnetic materials [79] has some characteristic properties, e.g., the effect of the enhancement of the exciting field on the magnetization reversal of domains, and was observed considerably later [80].

At the very beginning of the 1950s, some AFMR effects were studied (E Traunson et al., T Okamura, and other researchers). The translations of these works into Russian were published in Ref. [75, pp. 203–207]. In 1952, N Poulis and G Hardeman studied in detail NMR in antiferromagnets. The first studies of AFMR in the Soviet Union were carried out by the group led by A S Borovik-Romanov in the 1950s; in the 1960s, L A Prozorova joined these studies in which the results that have a fundamental value were obtained.

From 1949 to 1950, there was discovered a modification of the magnetic resonance of nuclear spins in the absence of an external magnetic field—the so-called purely quadrupole nuclear resonance (H-G Dehmelt, H Krüger [81]). More than 90 stable and long-lived nuclides (isotopes) possess electrical quadrupole moments and their spins I experience electrical quadrupole interactions (EQIs) with the environment (inhomogeneous crystalline and molecular fields). In the absence of a magnetic field, the NQR (in the presence of a magnetic field, the NMR) of such nuclides gives up to $2I + 1$ lines; however, the number of lines in the case of axial symmetry of the environment decreases (degeneracy). The discovery of the NQR of different nuclides started from the chlorine ^{35}Cl and ^{37}Cl isotopes [81]; then, its study was continued with the bromine and iodine ^{79}Br , ^{81}Br , ^{127}I isotopes, etc. (see Table 1). The spin Hamiltonian of nuclei with EQI (NQR and NMR quadrupole nuclei) is characterized by the presence of terms that depend on the squares of the spin projections (as for EPR in a zero field or EPR in the case of $S \geq 1$).

It would be desirable to divide the description of progress in the studies of magnetic resonance into three subsections: the formation of theoretical ideas, experimental methods, and practical applications of magnetic resonance. However, A Abragam in the preface to the ‘bible’ of NMR [13, Preface] noted that a specific feature of this field of science consists in a very close connection between theory and experiment, and this leaves no place for a theory that cannot be checked by experiment, or for an experiment that does not have a theoretical interpretation. We will devote Sections 2.6 and 2.7 to the most general description of theoretical works in the field of magnetic resonance approximately between 1948 and 1978 and to the development, in this period, of experimental magnetic resonance methods. But in conclu-

²¹ A significant contribution to the investigations of FMR was made at the early stage by C Kittel, R Bozorth (United States), and their colleagues (see Refs [75, 76]). A contribution of K Gorter's group (the Netherlands) to the discovery of AFMR is also worthy of mention. In the Soviet Union, investigations of high-frequency magnetic dispersion in ferro- and ferrimagnets, started by V K Arkad'ev, were continued by L A Fomenko, G V Skrotskii, et al. (see references cited in Refs [66, 75, 76]).

sion of Section 2 we will dwell on the consideration of the advancement of several special and important areas.

2.6 Developing the theory of spectral and relaxation parameters

The first steps in the theoretical interpretation of spectral and structural correlations were the confirmation of the significant role of electron–electron correlations in electron–nuclear hyperfine interactions and the development of the theory of the effective spin Hamiltonian [68, 70, 82]. Approximately at the same time, there appeared basic works on the spectral theory of the systems of nuclear spins with dipole interactions (G E Pake [83], J H van Vleck [44], and some others). Then, there appeared the first works on the theory of nuclear spin shielding by electron shells in molecules, and the shielding of the nuclear electrical quadrupole moment by electron shells (Sternheimer [84]). The author of the first works on the theory of electron shell shielding of the Zeeman interaction of nuclear spins (chemical shift), which is proportional to the quantizing field $-\sigma H_0$, and the indirect spin–spin interactions J (ISSIs)²² between the nuclei was N Ramsey [85, 86].

Quite rapidly (already in the early 1960s), the successes of experiments on NMR stimulated the development of computational methods which subsequently allowed *ab initio* calculations (see Section 3) of σ and J . The methods under consideration were based on the further development of the Hartree–Fock theory of the self-consistent field taking into account electron–electron correlations and the application of efficient trial-and-error methods of choosing atomic functions. The methods of *ab initio* quantum-mechanical calculations of the parameters of the spin Hamiltonian were continuously improved from the very beginning of the era of magnetic resonance. For the NMR of molecules, algorithms based on the ideas of the Hartree–Fock theory of the self-consistent field were developed by J Pople (see, e.g., Refs [87, 88]). A large contribution to the development of the optimum basis of atomic wave functions for the solution of similar problems was made by J Slater [89].

A significant place in the literature on the applications of NMR was at one time (1950–1960s) occupied by work on the approximate calculations of complex NMR spectra of multi-spin systems (they are widely reflected in monographs on high-resolution NMR (see references cited in Refs [66, 67]). Gradually, with the increasing strength of the technically accessible polarizing fields, these problems lost their urgency.

In the theory of electron spin–lattice relaxation, the first steps were made by I Waller [90], J van Vleck [34], and others even before the observation of magnetic resonance in the substance. The Oxford school of EPR researchers also made a contribution to the relaxation theory (see Refs [11, 67]). The processes which cause this relaxation are connected with three modes of spin interaction with the lattice vibrations (spin–phonon interactions): via direct resonance; the two-phonon mode of Raman scattering, and two-phonon (Orbach–Aminov) resonance (see, e.g., monographs [15] and [11, 20]). S A Al'tshuler was the first to indicate the possibility of spin–spin interaction with external phonons [acoustic paramagnetic resonance (APR)] [91]. Soon, APR was revealed in experiments [92].

²² The magnitude of the ISSI remains unaltered with a change in the magnitude of the quantizing field, but the main thing is in that the ISSI is effected only in the presence of electron coupling between the atoms that are the hosts of the nuclei, i.e., it is indirect, in contrast to the direct dipole–dipole interaction.

The first serious work on the theory of nuclear spin–lattice relaxation is related to N Bloembergen's name (see the BPP work [64] on relaxation in liquids, and his work [93] on relaxation in crystals). The fundamental achievement of the first steps in the relaxation theory of nuclear spins was the explanation of the role played in the relaxation of nuclear spins by unpaired electron spins of paramagnetic impurities. Bloembergen also suggested an idea on the transfer of spin excitation over the crystal to the 'relaxation centers' (i.e., to paramagnetic impurities) via the DDI mechanism. This process was called spin diffusion. One of the most beautiful approximations in the theory of this process belongs to the Georgian physicist G R Khutsishvili (see his review [94]).

The relaxation mechanisms are so diverse that we cannot enumerate here even the most important situations (see, e.g., Refs [11, 13, 15]). We might only indicate the fundamental role of cross relaxation (see, e.g., Ref. [95]) and also recall Hubbard's work [96] (it did not fall into the monograph [15]) concerning the spin-rotational relaxation of nuclear spins, which plays a noticeable role in gases and liquids for light molecules and for heavy nuclei (beginning already with ¹⁹F).

A separate direction in the theory of magnetic resonance related to the relaxation theory was the development of ideas of the spin temperature by A Abragam, A Redfield, B N Provotorov, and M Goldman [97–100], which is especially important for an analysis of complex systems with different spins in solids.

Among the most frequently cited early work concerning the theory of line shape, we should mention work by Vangsness and Bloch [101], Kubo and Tomita [102], and Anderson and Weiss [103]; of later works, those by Zwanzig [104] and Mori [105].

2.7 Formation of experimental magnetic resonance methods

The development of the applied research into magnetic resonances was determined by progress in the field of experimental technology. The oscillator response technique (see, e.g., Refs [42, 49, 50]) rapidly exhausted itself, since the connection between oscillatory systems of spins and the oscillator itself ('pulling') leads to a broadening of spectral lines and a reduction in the spectral resolution. In the high-resolution magnetic resonance, balanced methods with sweeping and modulation of the magnetic field (or frequency) became dominant. Finally, in experiments with pulsed switching-on of the exciting field the most efficient scheme proved to be a receiving circuit with one coil. This coil plays the role of both transmitting and receiving coils. This scheme of NMR experiments with an induction monitoring is shown in Fig. 6.

In the pulsed method with a subsequent Fourier transformation, this scheme became adopted once and for all. In experiment, the spectrometer directly records the decaying signal of free induction (free induction decay, FID) or the interferogram (sum of oscillations at different frequencies).

The design of experiments on EPR observing, as a rule, at higher frequencies than NMR (see Fig. 4), from the late 1940s was based on the waveguide–resonator technique (resonators with distributed parameters) functioning in different ranges of microwave frequencies: 10 GHz, 40 GHz, etc. In the first decade of NMR studies, E Hahn, H Carr, E Purcell [106, 107] and others developed the spin echo methods (recovery of the coherence of signals from different parts of a sample after damping with the aid of a repeated pulsed excitation) (see

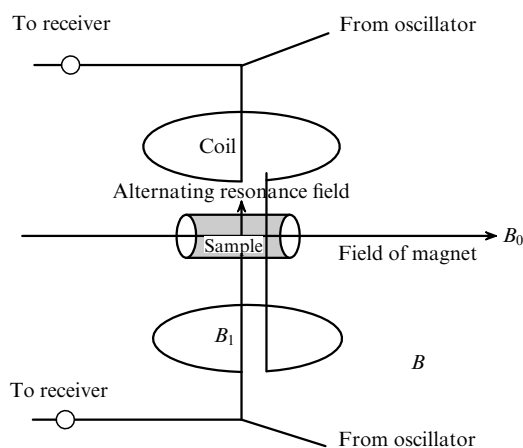


Figure 6. A schematic of an NMR experiment (induction method) on meter waves (frequencies on the order of 10^2 MHz). Shown are a sample, an external magnetic induction B_0 , the exciting and receiving coil and its magnetic induction B_1 , and connections with the receiver and the oscillator.

Refs [19, 64, 65]). The ‘echo’ principle obtained substantial development in the transition from the continuous excitation of resonance to the pulsed procedure [19, 108] and also found a certain application in the EPR technology [109].

In 1969 (with priority from 1965), two research workers at Varian, W Anderson and R Ernst (who was then a young fellow from Switzerland), were given a patent for the pulsed excitation of complex broadband high-resolution NMR spectra with a subsequent Fourier transform [110]. The revolutionary nature of this modification of the magnetic resonance technique, which replaced sequential spectral analysis by a simultaneous analysis over the entire frequency range $\Delta\Omega$, is evident from a statement by the outstanding experimenter of the firm J Shoolery: “Russell Varian looked at these spectra (in which 90% of the frequency range were filled with noise signals and only rare spectral lines were observed against the background of these noise) and asked: ‘And whether it can be done so that the basic time of the work of the spectrometer would spent on the observation of spectral lines rather than noise?’ And he was right...”²³

The simultaneous excitation of the entire spectrum using a pulse with a duration of $1/\Delta\Omega$ replaced the continuous sweep in the range $\Delta\Omega$. This gives a gain in the time of the experiment of $\Delta\Omega/\delta\omega$ times without a loss of sensitivity, or in the signal-to-noise ratio of $\sqrt{n} = \Delta\Omega/\delta\omega$ times, where $\delta\omega$ is the average line width in the spectrum, and n is the number of repeated pulses. At present, the concept of the Fourier transform for ‘neophytes’ in NMR has become inseparable from the resonance itself. Even educational sites on NMR begin with a portrait of J B J Fourier whose famous theorem found understanding among new admirers (chemists), previously distant from spectra and their analysis.

The most important factor in increasing signal-to-noise ratio is the growth of the polarizing field. Indeed, in the case of induction recording of a signal, the signal-to-noise ratio is $S/N = \text{const } H^\alpha$, where $\alpha = 3/2$ to $7/4$ [13, Chapter 3, Section 11; 14] (see Section 3.7). But it is still necessary to ensure that

the instrumental bandwidth of the signal does not increase with increasing field strength. This requires an ever more precise correction of the spatial inhomogeneity of $H(x, y, z)$. The relative resolving power of the first Varian commercial NMR spectrometer in 1956 was about 10^8 , and this value has grown since then by an order of magnitude with an increase in the working frequency by the end of the 20th century by a factor of 20–30 (and in the sensitivity, by three orders of magnitude).

From 1964–1972, in the technology of NMR one more revolution occurred connected with the replacement of magnets with an iron core (fields up to 2.35 T) by superconducting solenoids (fields from 4.7 T to 11.7 T and later even still stronger). The growth in the field strength and in the resonance frequency made the main contribution to the progress of NMR (and also EPR) technology. This progress ensured, in addition, a serious simplification of the structure of complex spectra²⁴ and the elimination of random line overlaps, which created conditions for applying two-dimensional methods of information readout in multispin systems (see below). The cooling of the receiving circuit of the sensor by liquid helium (cryosensor technology) makes it possible to lower the noise level by almost an order of magnitude and thus again to increase S/N. Finally, the last couple of decades of progress in this field have also passed under the sign of the displacement of analog units by digital ones.

The magnetic resonance technique began to be in significant demand from the late 1950s because of developments at the pioneer of NMR instrument manufacturing, the Varian firm (United States), and its successful competitors, Bruker SpectroSpin (Germany, Switzerland) and the Japanese firm JEOL. A significant contribution to the development of NMR technology in the countries of the Council for Mutual Economic Assistance (COMECON) was introduced by the Czech firm Tesla–Brno. In the arsenal of NMR spectroscopy there are empirical spectrum–structure correlations and methods of quantum-chemical calculations of the spin Hamiltonian parameters (see Section 3). The first correlations between the structures of organic compounds and chemical shifts of protons were found by Shoolery [111], and for the rare isotope of carbon ^{13}C these were revealed by Holm [112] and Lauterbur [113].

Already in the first decades after the discovery of NMR a method of dynamic NMR was developed, based on an analysis of the line shape function for complex (multispin) spectra in the presence of reversible chemical transformations (see, e.g., Ref. [114]). Both the rapid relaxation of spin B, interaction with which determines the line splitting of spin A, and the rapid reversible reaction between states with different NMR spectra lead to the formation of a completely new spectrum (roughly speaking, to a line broadening and then to a confluence of lines in the spectrum). An auxiliary method in the high-resolution NMR spectroscopy of liquids became the method of lanthanide-based paramagnetic shift reagents [115]. An important avenue of studies were NMR and EPR studies of mesophases (liquid crystals and molecules partially oriented in a solution). Great attention was paid to studies of the effects of isotope substitution in NMR and EPR, and some others.

Methods based on the use of pulses of the polarizing-field gradient for restoring the standard initial conditions have

²³ This was J Shoolery’s address at the Institute of Virology of the USSR Academy of Medicine on the first exhibition of Varian devices in the Soviet Union in the summer of 1967 (I quote this from memory).

²⁴ This can be shown using the perturbation theory when calculating the spin Hamiltonian self-energies.

been successfully developed [116], leading to the destruction of coherence due to rapid diffusion in the inhomogeneous magnetic field; subsequently, these methods became the basis for diffusion-ordered spectroscopy (DOSY).

The application of superconducting quantum interference devices (SQUIDS) in NMR and EPR technology for registering the magnetic flux induced by a spin system in comparatively weak magnetic fields ($B \leq 0.6$ T) also makes it possible to increase the sensitivity for the recording of magnetic resonance signals (see an exhaustive review in Ref. [117]). Receiving devices which use SQUIDS became widely accepted in the late 1970s–early 1980s predominantly for studying NMR of ^3He , ^1H , ^2H , and other nuclei at low and ultralow temperatures.

Studies of EPR spectra and relaxation were mainly conducted using spectrometers produced by Varian and Bruker SpectroSpin, and in the Soviet Union the domestic spectrometer RE-13, one of the most successful Soviet instruments, was also employed. Notice here also the early successes of EPR in the selection of systems for masers which were employed in the radar of cosmic objects [118]. The general tendency of strengthening the polarizing field was characteristic of EPR spectroscopy as well. But systems investigated by EPR are mainly characterized by an inhomogeneous line broadening (the concept of which was introduced by Portis [119]). The inhomogeneous broadening is also determined by, among other factors, the spread of g factors in the sample, which makes the increase in H_0 in the case of EPR not as advantageous as in high-resolution NMR. But an increase in the frequency of EPR was favorable for all systems with $S \geq 1$ and with significant magnitudes of other parameters that influence EPR in a zero field.

Problems in the development of experimental (and theoretical) FMR and AFMR methods were reflected in the monographs by S V Vonsovskii [120], M I Kaganov, and A G Gurevich, and the development of NMR method in ferromagnets was described by E A Turov and M P Petrov [79].

The development of NQR technology from the very beginning rested on the method of pulsed excitation with a Fourier transformation in combination with the sweeping of the carrier frequency [12, 121].

2.8 History of nuclear magnetic resonance in solids

NMR lines in solids are wider than those in liquids by many orders of magnitude, and frequently they have a structure similar to the Pake doublet, and so forth [13, Chapter 7]. The reasons for this proved to be anisotropic spin–spin interactions (DDIs and EQIs, and partly CSs) which are averaged in liquids as a result of the rapid motion of molecules. The (secular) part of dipole–dipole interactions commutating with the Zeeman Hamiltonian (1.3) determines the width and contour of spectral NMR lines, in particular, the value of the second moment of lines in rigid structures [44] and, according to the Fourier theorem, the decay of the signal of free induction as well. If the bulk density of spin carriers is significant, then the line shape and the SSIs are determined by dipole–dipole interactions.²⁵ The secular part of the operator

of DDI between two spins S and I has the form

$$\frac{\gamma_S \gamma_I \hbar^2}{r_{SI}^3} \left[S_z I_z + \frac{1}{4} \delta_{SI} (S_+ I_- + S_- I_+) \right] (3 \cos^2 \theta - 1), \quad (2.8)$$

where the operators of spin projection are used, for example, $S_z, S_{\pm} = S_x \pm iS_y$, $\delta_{SI} = 1$ at $S = I$, $\delta_{SI} = 0$ for $S \neq I$, where r_{SI} is the distance between spins S and I , and θ is the angle between the spin vector \mathbf{r}_{SI} and the direction of the magnetic field (z -axis).

The dependence of the DDIs on the orientation of spin–spin vectors relative to the direction z of the quantizing external magnetic field²⁶ [see formula (2.8)] makes it possible to artificially manipulate the contribution from the secular part of the DDI to the line width. Already in the first two decades after the discovery of NMR there were found three methods for eliminating DDI. The first was the rotation about the axis directed at a ‘magic’ angle $\varphi_m = \arccos \sqrt{1/3}$ to the z -axis, which reduces to zero the dipole line width if the frequency of rotation is $\omega_{\text{rot}} \gg \omega_{\text{dd}}$, where ω_{dd} is the DDI energy in the units of frequency [122]. The second was the rotation in a ‘spin space’ (see Refs [5, Chapter 4] and [123]), i.e., the magnetic resonance pulsed excitation of precession about alternately different axes (for example, x, y, z), which may lead to a situation where the average value of $\theta = \varphi_m$ and DDI in the first approximation will tend to zero. The third method was connected with the elimination of interactions with unlike spins, i.e., with the decoupling effect in the case of double resonance (see Section 2.9). Later on, different efficient combinations of these methods were developed.

For nuclei with $I \geq 1$, quadrupole interactions move to the foreground, which split the NMR lines in comparatively strong fields (when the EQI is nevertheless much less than the Zeeman interaction). Furthermore, the imperfection of the structure of solids (e.g., a polycrystalline structure) leads to a spread of the contributions to NMR frequency caused by EQI over the sample and to an inhomogeneous line broadening. The respective studies were performed already at the end of the 1950s (see Ref. [124, pp. 321–348]). The quantum-mechanical perturbation theory with a value of the cyclic Larmor frequency $\nu_L = \gamma_I H_0 / (2\pi)$ and an NQR frequency (in the case of axial symmetry) equal to

$$\nu_Q = \frac{3e^2 q Q}{2hI(2I-1)},$$

where Q is the quadrupole nuclear moment, and q is the electric-field gradient at the nucleus, gives for the first-order corrections $\delta\nu^{(1)}$ to the NMR frequency the expression

$$\frac{\nu_Q}{4hI(2I-1)} (3 \cos^2 \theta - 1) \left[m^2 - \frac{1}{3} I(I+1) \right], \quad (2.9)$$

where m is the magnetic quantum number corresponding to the upper level for the transition, and θ is the angle between the axis of the EQI tensor and the direction of the magnetic field. In the second order of perturbation, frequency

²⁵ DDIs for the spins of ^1H that are present in a concentration of 10^{22} cm^{-3} (e.g., in polyethylene) give in the spectrum of wide lines a contour of the line of proton magnetic resonance (PMR), which has a root-mean-square width of up to 5×10^4 Hz. The width of the NMR lines of fluorine in calcium fluoride (CaF_2) which contains the same concentration of ^{19}F is only 12% less at some orientations of the crystal.

²⁶ Formulas for the quantum operator of DDIs, analogous to Eqn (2.8), were being used already at the beginning of the 1930s (see, e.g., Refs [35, 90]).

correction $\delta v^{(2)}$ is described by the expression*

$$\delta_m^{(2)} = \frac{v_Q^2}{3v_L} m \left\{ \frac{3}{2} \cos^2 \theta (1 - \cos^2 \theta) [8m^2 - 4I(I+1) + 1] \right. \\ \left. \times \frac{3}{8} (1 - \cos^2 \theta)^2 [-2m^2 + 2I(I+1)] \right\}. \quad (2.10)$$

The rotation of the sample at ‘magic angles’ eliminates the EQI as well. Correction (2.9) tends to zero upon the rotation of the sample as a whole at the same angle as that corresponding to the elimination of the DDI, i.e., at $\varphi_m = \arccos \sqrt{1/3}$. Correction (2.10) tends to zero at $\varphi_m' = 90^\circ$.

The first attempts to eliminating and simultaneously determining the EQI in anisotropic samples were based on a combination of the specimen rotation and the ‘rotation in spin space’, i.e., a pulse action; simultaneously, a proton–carbon cross polarization could also be applied (see below).²⁷ Methods involving the simultaneous mechanical rotation of a sample at two angles arose only at the end of the 1980s [126]. According to formula (2.10), the rotation of the sample is efficient in the second order only in high polarizing fields. For many nuclides, the EQIs are so high that it is difficult to reach an angular frequency that can sufficiently exceed $\delta v^{(1)}$ and $\delta v^{(2)}$ (i.e., is greater than 2×10^4 Hz). However, there do exist nuclides for which the EQI can sometimes be eliminated (for example, ²⁷Al [127]). (The NMR of quadrupole nuclei is considered in more detail, e.g., in the review written by P Man [54, Vol. 6, pp. 3838–3848].)

For chemical applications, chemical shift is the most important interaction. The problem of establishing the molecular structure of solid phases began to be solved successfully at the borderline of 1960s and 1970s by determining and interpreting sets of CSs in these phases. The EQI and DDI between closely spaced nuclei (in a molecule) are much greater than the differences between the CSs (especially between the CSs of protons). Therefore, the task is reduced to the elimination, at least partially, of the DDI and EQI. The chemical shift is also anisotropic; however, the trace of the shielding tensor, which determines the CS, is not equal to zero, $\text{Sp}|\sigma| \neq 0$, in contrast to those for the DDI and EQI tensors; it cannot be brought to zero by rotation, but only tends to the value $(1/3)\text{Sp}|\sigma|$ (see Appendix to Mehring’s monograph [5]). Owing to the efforts of many researchers (note especially the schools of J Waugh and A Pines, U Haeberlen and M Mehring, E Lippmaa and A Samoson, which, by the way, always closely collaborated), an area of high-resolution NMR in solids that is very important for the chemistry of organic and inorganic polymers, silicates, and other compounds was formed.

The possibility of manipulating parameters of the spin Hamiltonian [here, we can speak of not only DDI, but also EQI and CS (see above)] is a unique feature of magnetic resonance, which allows a physically real transfer of a system to a rotating frame of reference [recall expression (1.5)], where the value of the effective field can change by several orders of magnitude.

* Formula (2.10) was refined by the author for the English translation.

²⁷ The variety of pulse sequences aimed at extracting different information about spin systems of any kind is so great that the well-known specialist in NMR R Freeman called these methods of magnetic resonance a ‘spin choreography’ [125].

The most important achievements of ‘spin choreography’ are the spin echo methods. The pulsed actions of a magnetic field with a resonance frequency can first assign and then (after the decay of the signal) restore the coherence of the precession of quasi-isolated spin systems not only in an inhomogeneous external magnetic field (Hahn nuclear spin echo [106]), but also in effective local fields of spin systems coupled via DDIs (magic echo discussed by W-K Rhim, A Pines, J Waugh [128]). (For details, see the monograph by Abraham and Goldman [129, Chapter 1].)

The DDIs between the spins, as well as the EQIs, result in emerging so-called forbidden transitions, multiquantum transitions, and ‘multiquantum coherence’ (see Refs [19, 108]), the excitation and detection of which require special procedures.

2.9 Development of methods of double resonances, dynamic polarization, and multidimensional spectroscopy

The possibility of a wide application of double resonances remained almost exclusive to magnetic resonance owing to the variety of types of spin carriers and the relative narrowness of the lines. These are the so-called double electron–electron, electron–nuclear, nuclear–electron, and internuclear (including also magnetic–quadrupole) resonances (ELDOR, ENDOR, NEDOR, partially INDOR). The double resonances either reveal interactions between spins of different types or between spins of one type located in different environments [hence, the possibility of two-dimensional spectroscopy (see below)] or make it possible to indirectly observe the resonance of such a spin, for the direct observation of which the sensitivity or resolution of the ‘monoresonance’ method is insufficient. Double optical magnetic resonances (DOMRs), for the first time revealed in gases [17], are now observed in crystals as well.

Subsequently, double resonance methods were rapidly developed. In Pound’s experiments on the relaxation of spins with $I > 1/2$ [130], there were demonstrated the ‘pumping’ effects which were later realized by N Bloembergen, A M Prokhorov, and others in masers (including those designed on paramagnetic systems) and lasers.

In 1953, the Overhauser effect was discovered—the first in a series of subsequently revealed numerous effects of double nuclear–electron resonances and transfer of polarization from a system of spins S with a larger γ_S to a system of spins I with smaller (in magnitude) γ_I (usually, from electron to nuclear spins), i.e., a dynamic nuclear polarization (DNP) upon EPR saturation [131, 132]. Soon, A Abragam and I Solomon [133] showed that the effects of the transfer of polarization appear not only in metals and not only in the presence of hyperfine (scalar) interactions between S and I spins (as was supposed in paper [133]) but also possibly in the case of rapidly changing DDIs between unlike spins, as well as between like spins (or between spins with close values of γ_I). The coefficient of enhancement of the magnetic moment M (polarization) of spins I upon saturation of the resonance of spins S is written out as

$$E_p = 1 + f \frac{\gamma_S}{\gamma_I}, \quad (2.11)$$

where $E_p = M/M_0$, M_0 is the thermal equilibrium value, and the factor f depends on the contribution of the joint reorientation of S and I spins to the relaxation rate. According to formula (2.11), under favorable conditions the

polarization and the NMR signal can grow by a factor of several hundred (to 660 upon scalar interaction, and to 330 upon dipole interaction for ^1H). The nuclear Overhauser effect (NOE) between dipole-coupled spins of the same type leads, according to formula (2.11), to a limiting value of $E_p = 1.5$, since for the DDI the maximum value of f is equal to 0.5 [13, 133].

At approximately the same time, the first experiments were performed on double resonance for the purpose of simplifying and interpreting the high-resolution NMR spectra in liquids. Varian's researcher V Royden [134] used for the first time a decoupling of the spin–spin interaction for the indirect (in the resonance of ^1H) determination of the NMR frequency of the nucleus (^{13}C) that was not observed directly in the spectrum (DNR of $^1\text{H} - \{^{13}\text{C}\}$).

For the first time, double nuclear resonance between identical nuclei (homoresonance decoupling and other effects of the weaker irradiation field in the proton magnetic resonance $^1\text{H} - \{^1\text{H}\}$) was used by Bloom and Shoolery [135]. Since 1960, the double resonance in high-resolution NMR spectra of multispin systems with a significant number of nonequivalent groups of spins has been studied in many laboratories around the world. One of the pioneers of the wide application of these methods (weak perturbation of the spectrum, or tickling, partial or complete decoupling, or 'shaking' of the ISSI, according to monograph [13]) was R Freeman [136]. Among those who employed double nuclear resonance in high-resolution NMR already in the 1960s were also J Baldeschwieler, R Kaiser, D Elleman, E Lippmaa, V F Bystrov, and many others. The most common methods by the end of the 1960s were the DNR of $^{13}\text{C} - \{^1\text{H}\}$ and $^1\text{H} - \{^1\text{H}\}$.

Up to the 1990s, two types of double-resonance methods, based on the saturation and transfer of polarization (NOE) and on local or total perturbations of the high-resolution spectrum, where between the precession of unlike spins there is a correlation caused by the ISSI and where the transfer of coherence is possible, were successfully realized in the methods of two-dimensional NMR spectroscopy [19] (see below).

The double-resonance methods made it possible to indirectly observe the resonance of those types of spins whose direct observation is impossible because of the lack of sensitivity, resolution, or other technical capabilities of the 'monoresonance' method. The most important of such methods proved to be the method of electron–nuclear double resonance (ENDOR) in EPR, which for the first time was realized in G Feher's work on extrinsic semiconductors [137] and later in dielectrics [11, 138]. The indirect observation of the passage through the line of the magnetic resonance of spin I is performed by observing the changes in the intensity of a signal of spin S whose relative sensitivity (cf. Fig. 4) can be considerably greater than that of I ; the very fact of the presence of coupling between the spins is established, and the value of its energy and relative sign of this energy in comparison with the energy of other spin–spin interactions is determined.

As was indicated by R Ernst in his Nobel Lecture [108], referring to the communication of the Belgian researcher J Jeener at the Conference in Basko Polje (1971), it was Jeener who for the first time proposed, on the basis of two-pulse methods of excitation of NMR signals, to move to two-dimensional spectroscopy. The two-dimensional representation of the spectrum of a multispin system becomes possible

when there exist interactions of different spins (e.g., i and j) between themselves. In this case, the sweeping of the excitation frequency in the interval of frequencies $\Delta\omega_i$ of one of the spins is replaced by a step-by-step change in a time interval, $T + k\tau$, between the exciting pulses in a series of experiments, $1 < k < n$. Thus, the number of experimental points becomes proportional to the ratio $\Delta\omega_i \Delta\omega_j / (\delta\omega \delta\omega_j)$, where $\delta\omega \approx 1/\tau$ is the required line width of spin resonance or the quantity that is inverse to the time step τ between the measurements or the delay time between the pulses. For data processing, a double Fourier transform is required.

The methods of two-dimensional spectroscopy have been described in the literature in great detail; we, therefore, only recall the role of the pioneers (see, e.g., some of the first works on two-dimensional heteronuclear correlation spectroscopy (hetero-COSY), homonuclear correlation spectroscopy (homo-COSY), and homonuclear exchange spectroscopy based on the NOE (homo-NOESY) [139–141]). Some typical results of such experiments are shown in Fig. 7. They correspond qualitatively to the picture of a double resonance of each of the spins excited in the frequency interval $\Delta\omega_i$ with each of the spins excited in the interval $\Delta\omega_j$.

These intervals can lie in completely different frequency ranges (hetero-COSY, Fig. 7a) or, on the contrary, coincide (homo-NOESY, Fig. 7b). To those pairs of spins that exhibit ISSIs between themselves ($J_{ij} \neq 0$), there correspond peaks in the two-dimensional COSY spectrum (Fig. 7a). To those pairs that experience cross relaxation as a result of DDIs, there correspond peaks in the NOESY spectrum (Fig. 7b). These methods in diverse modifications received wide acceptance by the 1990s.

From the 1960s–1970s, in connection with the search for objects for polarized nuclear targets, significant progress was achieved in the examination of the dynamic nuclear polarization (DNP) upon EPR saturation at low temperatures (liquid-helium temperatures) in solids, in which the EPR lines are broadened nonhomogeneously and the most important role in the thermal contact between different spin subsystems belongs to DDIs.

Abragam and Proctor [142] and later Erb et al. [143] showed the possibility of a dynamic polarization of nuclear spins upon saturation of forbidden EPR transitions at frequencies of $\omega_S \pm \omega_I$ (satellites of the line of spins with $\gamma_S \gg \gamma_I$), which was called the solid effect. At a sufficiently large concentration of electron spins and significant widths of the EPR line, we have $\delta\omega_S \gg \omega_I$ and the solid effect as the DNP method is replaced by the mechanism of energy transfer from the dipole–dipole reservoir (DDR) of spins S , postulated in the work of Provotorov²⁸ [99], to the nuclear Zeeman reservoir (NZR) of spins I , i.e., to the mechanism of thermal mixing of DDR and NZR upon EPR saturation [21, pp. 73–86; 129, Chapter 6]. These methods give, with a lucky choice of objects and conditions, a polarization of nuclei close to 100% [146].

The basic mechanism of the elementary acts that lead to DNP upon saturation of wide inhomogeneously broadened

²⁸ For the historical aspect of the contribution made by B N Provotorov and his successors (V A Atsarkin, M I Rodak, A E Mefed, and some others), see Ref. [144], and for a description and estimation of this contribution by A Abragam and M Goldman, see, e.g., Refs [20, 100, 129]. However, it was Landesman and Goldman [145] who were the first to use the term 'thermal mixing' for describing double NQR–NMR, namely, $^{35}\text{Cl} - \{^1\text{H}\}$.

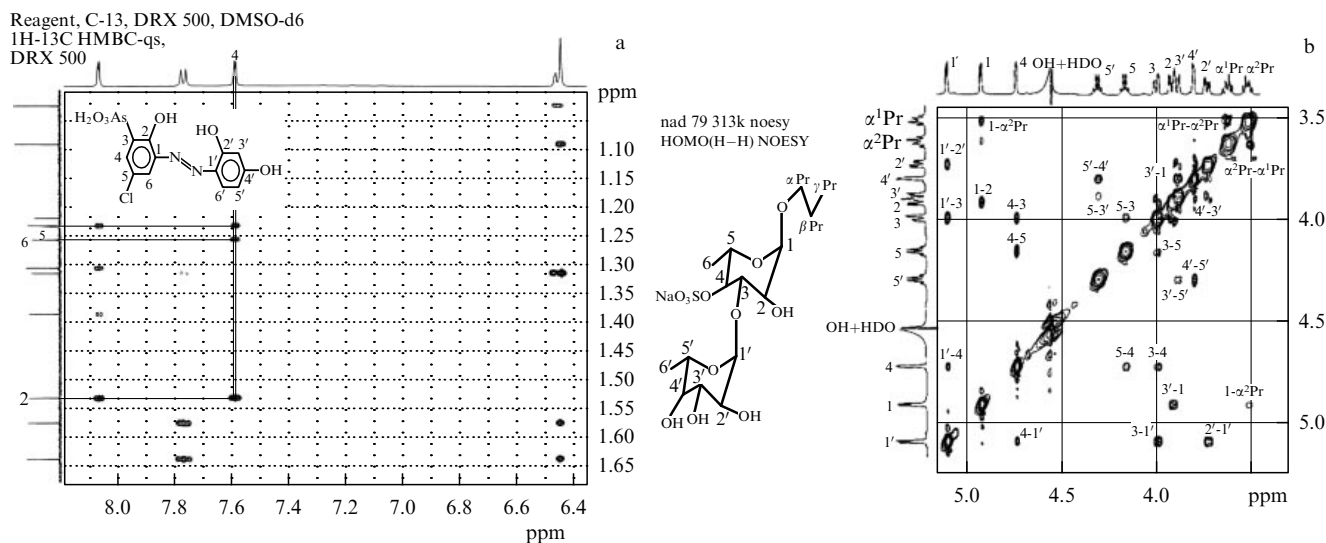


Figure 7. (a) A hetero-COSY ^{13}C – ^1H spectrum of an azo compound, which indicates the existence of scalar interactions between the ^{13}C and ^1H nuclei and, thus, makes it possible to identify the lines in spectra of both nuclides (along the ordinate axis, the spectrum of ^{13}C , and along the abscissa axis, the spectrum of ^1H are plotted). (b) A homo-NOESY ^1H – ^1H spectrum, which indicates, in particular, the mutual spatial proximity of some protons in the disaccharide structure (along the coordinate axes, the same ^1H spectra). In both (a) and (b) figures, the measurement units along the axes are millionth fractions of frequency (ppm). The spectra have been obtained in the Laboratory of Nuclear Magnetic Resonance at the N D Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences by (a) Yu A Strelenko, and (b) A S Shashkov.

EPR lines was assumed to be the effect of electron–nuclear cross relaxation (ENCR, or cross effect) [147] (see Section 3). It is difficult to construct an appropriate theory of ENCR under the conditions of competition with other mechanisms of electron cross relaxation and nuclear–electron relaxation, as was shown in Ref. [21]. But for a thermodynamic consideration of the thermal mixing mechanism for some systems this is by no means necessary (see Ref. [21]). And it was only recently that chemists from MIT ‘designed’ a system (a frozen solution of biradicals [148]) in which the ENCR effect could be studied in a ‘pure’ form.

The transfer of polarization from one type of spins to another (in fact, again thermal mixing) is widely used in the NMR spectroscopy of liquids and solids for increasing sensitivity in the observation of NMR of nuclides with small γ_I . J Waugh called this method of acting on the nuclear moments ‘spin alchemy’.²⁹ To observe in solids rare spins I (as, for example, in the case of the minor isotopes of ^{13}C , ^{29}Si , and ^{43}Ca with their natural abundances of 1.1, 4.7, and 0.135%, respectively), which, in addition, have comparatively low γ_I , in the presence of major isotope spins with a significant γ_S , the method of I – $\{S\}$ decoupling with a rapid rotation of the specimen as a whole at a magic angle is now used, which creates conditions for the transfer of polarization via a mechanism analogous to NOE in liquids (see Ref. [5]). This combination of cross polarization with a rapid rotation of the specimen at an angle φ_m to the field direction is called

cross polarization–magic angle spinning, CP–MAS), which, since the 1980s, is used in commercial NMR spectrometers for studying solids.

Two-dimensional methods of registering correlation and dynamic (exchange and relaxation) coupling between nuclear spins in solids (most frequently under the action of multipulse sequences, i.e., rotations in the spin space and/or the rotation of the entire specimen) have also received wide acceptance [19, Chapter 7, Sections 3, 4; Chapter 8, Sections 5, 6; Chapter 9, Section 10]. The first experiments on correlation spectroscopy in solids were realized from 1971 to 1983 (see, e.g., Ref. [150]). The procedures for determining the relationships between the orientations of the principal axes of DDI, EQI, and CS tensors in powder specimens are interesting but complex [151]. The simplest information that is accessible in the two-dimensional representation for spectroscopy such as NOESY is the separation, in a spectrum, of lines of individual molecules or individual monomeric units in polymers (adjacent spins are coupled via DDIs, which is manifested in the form of cross-peaks in 2M-images [152]). The schools of R Ernst, A Pines, and others have been working in these areas. Already in the monographs [5, 19], various situations, problems, and related experimental methods were considered, and a vast bibliography was given.

2.10 Magnetic resonance and spin-controlled processes

The expansion of the frontline of studies into spin systems by the magnetic resonance methods demonstrated already in the 1950s that the field of application of magnetic resonance is not limited to studies of only substances in which the spins play a passive role of sensors that receive information about the processes occurring in condensed media. The application of magnetic resonances can not only reflect the course of a process, but also influence its direction (for example, the annihilation of an electron and a positron in positronium [153]). Later on, other processes became known, whose

²⁹ A Hartmann–Hahn condition [149] is known for a doubly rotating (with frequencies ω_S and ω_I) coordinate system: $\gamma_S H_{S\text{eff}} = \gamma_I H_{I\text{eff}}$ (where the subscript 1 points to the amplitude of the rotating field [cf. formula (1.5)]. According to J Waugh, this is the basic relationship of ‘spin alchemy’; if it is fulfilled, the NMR frequencies of spins of different elements can become, according to formula (1.5), equal to each other, which will ensure thermal mixing.

appearance itself and whose result depends on spin orientation (the reaction of a muon and an electron in muonium [154], etc., and finally some chemical reactions [for more details, see below]).

An effective method of registering spin-dependent interactions of neutrons with nuclei proved to be so-called pseudo-magnetic resonance, which is recorded as a change in the neutron flux for the magnetic resonance of nuclei interacting with neutrons [129, Chapter 7], [155].

The DNP methods are the base for the magnetic-resonance method of producing a spin phase transition in a quasi-isolated spin system, i.e., magnetic ordering (ferromagnetism and antiferromagnetism of atomic nuclei caused by their DDIs). The method relies on the saturation of the EPR of paramagnetic impurities (Abragam et al. [129, Chapter 6; 156]), which results in a fantastically low spin temperature—on the order of 10^{-6} – 10^{-7} K, corresponding to Curie–Néel temperatures for systems of nuclei with DDIs.³⁰

The effects of anomalous polarization of nuclear and electron spins were discovered in the 1960s in some chemical reactions when studying them by the EPR and NMR methods (as they say, ‘in the ampoule of the spectrometer’). For a while, empirical data were accumulated, and then, in the works of Kaptein and Oosterhoff [157], Closs [158], and finally Adrian [159], these effects were explained as being due to spin selection upon repeated collisions of radical pairs formed earlier as a result of the decomposition of singlet molecules. Some difficulties that were met in the explanation of the polarization effects in the course of multistage reactions with transformations of radicals between the pair production and radical collision were overcome in the work by den Hollander [160].

The understanding of the mechanism of evolution and selection of spin states in such reactions triggered the discovery of a number of interesting effects, e.g., the dependence of polarization on the magnetic field [161] (Molin, Sagdeev, Salikhov et al.), and the spin isotope effect [162] (Buchachenko et al.). A unique possibility of detecting magnetic resonance by measuring reaction yield (resonance yield detection of magnetic resonance, RYDMR) was revealed. This effect has been studied by E L Frankevich et al. [163] based on the example of the yield of photoluminescence in the interaction of paramagnetic excitons in aromatic hydrocarbons. Various techniques appeared for studying the dependence of the reaction yield on the magnetic fields strength (magnetic-affected reaction yield, MARY) (see, e.g., paper [164]).

The effects of singlet–triplet transitions in radical pairs under the action of magnetic interactions that are different for each of the partners—radicals most frequently serve as characteristic spin effects capable of determining the direction of chemical reactions of paramagnetic particles (pairs of free radicals, biradicals, and so forth). Upon a collision, for example, a singlet pair of radicals forms a stable molecule, while a triplet pair again ‘scatters’. This spin-controlled reaction can depend on the orientation of nuclear or electron spin; then, the states that are ‘active’ are accumulated in the appropriate reaction products and there

are impoverished states that are ‘passive’ with respect to the formation of this product.³¹ This is registered by the methods of, correspondingly, NMR or EPR of the reaction products [chemically induced nuclear polarization (CINP) and chemically induced electron polarization (CIEP)] [65, 93, 165]. The monograph [165] contains a vast bibliography and a description of the experimental and theoretical background of spin and magnetic effects in chemistry. The methods of CINP, CIEP [or, alternatively, chemically induced dynamic nuclear polarization (CIDNP) and chemically induced dynamic electron polarization (CIDEP)], MARY, RYDMR, and the magnetic resonance methods of observing the reaction yield depending on the isotopic composition enter into the arsenal of ‘spin chemistry’. A conceptual survey of its problems has been given by A L Buchachenko, E L Frankevich, and Ya B Zel’dovich in review [166].

3. Topical areas of studies and applications of magnetic resonance in modern natural science, medicine, and technology

The application-oriented trend in the development of the physics of magnetic resonance is obvious. The list of the 25 most frequently cited scientific papers on physics in the last quarter of 2005, according to Science Direct, contained two articles dealing with the application of magnetic resonance. There are several specialized journals devoted to magnetic resonance.³² Our selection of topical areas is certainly subjective, but in many respects it coincides with the topics of recent (2006–2008) EUROMAR conferences [167].

Note that all the known possibilities for the further development of magnetic resonance methods and their applications are being used quite efficiently at present.

3.1 Some problems in the physics of magnetic resonance

Studies of systems with a limited though significant number of spins ($N_S = 10$ – 100), which concern the problems of ergodicity and searching the facet between dynamic and statistical tasks, lead to problems in quantum computing [168]. Important conclusions can be obtained from studies of multiquantum coherence in such systems (see, e.g., Ref. [169]). Of great interest for researchers is also the facet between a group of interacting spins (an exchange cluster, or a molecular magnet) and a ferromagnetic (antiferromagnetic) domain (from the works we know of, see, e.g., Refs [170,

³¹ The state of a pair of radicals is determined by the relative phases of oscillations of the spin states of the pairs of the interacting particles in the time period between their collisions, when the exchange interaction between the spins of the pair is switched off, rather than by transitions under the action of perturbations (for more details, see monograph [165]).

³² See, e.g., *Journal of Magnetic Resonance*, *Applied Magnetic Resonance*, *Magnetic Resonance in Chemistry*, *Progress in Nuclear Magnetic Resonance Spectroscopy*, and *Solid State Nuclear Magnetic Resonance*. Papers on magnetic resonance are also published in the *Journal of Biomolecular Magnetic Resonance* and some others. There are also issued special journals devoted to NMR tomography (*Magnetic Resonance Imaging*, and others). Among the journals of a wide chemical, biochemical, and physical profile that publish appropriate papers on magnetic resonance we should mention *Analytical Chemistry*, *Angewandte Chemie*, *Chemical Physics Letters*, *Inorganic Chemistry*, *Journal of Molecular Biology*, *Izvestiya Rossiiskoi Akademii Nauk (Ser. Fizicheskaya, Khimicheskaya)*, *Uspekhi Khimii*, *Uspekhi Fizicheskikh Nauk*.

³⁰ Notice that temperatures on the order of 10^{-6} K for a macroscopic specimen as a whole are practically unattainable under terrestrial conditions in view of the presence of cosmic radiation and radioactive background.

171]). The problems of the magnetic resonance of collective excitations of multispin low-dimensional systems (spin liquids) depending on temperature and magnetic field strength are being actively developed (see, in particular, the works of V N Glazkov, A I Smirnov, and others, e.g., Ref. [172]).

Studies of spin diffusion, relaxation, and spectral-line contours in disordered spin systems are being carried out, for example, by F S Dzheparov [173] and colleagues. These studies concern the diverse effects observed in experiments on magnetic resonance, such as the transfer of polarization, the distortion of the shape of the resonance-line contour during the excitation in a narrow frequency range ('hole burning' in the contour of the line), a change in the shape of this contour on the line wings, etc. Low-dimensional systems, for example, linear chains of spins, are of threefold interest. First, here we frequently deal with systems accessible for both experimental and theoretical (computational) studies. Second, some of them are suitable, as is indicated, for instance in Ref. [174], for quantum computing. Third, detection of low-dimensional spin subsystems by the magnetic resonance methods can lead to important inferences about the electron structure and the nature of the properties of a substance, such as conduction, magnetic phase transitions, and some others.

Notice finally that in the school of B N Provotorov a perhaps most general theory of the NMR and EPR line shape applicable to crystals, polymers, and liquids was developed [175], but this theory had not obtained a sufficient reputation until now.

3.2 Newest applications of 'routine' methods of magnetic resonance in chemistry

Owing to the improvement in experimental methods and the theoretical interpretation of the spin Hamiltonian parameters, new horizons have opened before researchers in the field of chemistry. As an example, we can mention the determination of the structure of molecules of individual chemical substances from high-resolution NMR spectra. The productivity of devices developed by the foremost firms (instruments with a magnetic field induction exceeding 7 T) has grown to several hundred spectra (several hundred investigated substances) per day.³³ The interpretation of an NMR spectrum helps one to confirm or reject the tentative structure of a base material and to identify impurities that can hardly be distinguished with the aid of other methods.

NMR data have been included in the general techniques of correlation and logical analysis of data systems—from molecular weight to optical activity (see, e.g., Ref. [176]). The high-resolution NMR spectrum directly indicates the presence of structural fragments that contain nuclei whose resonance is observed in experiment. The NMR data point to the general type of fragment and make possible the determination of the environments of these fragments, in particular those that contain magnetic nuclei (dipole–dipole and indirect spin–spin interactions) (see Fig. 7). The influence of molecular fragments containing no resonant nuclei is reflected in the spectrum indirectly, due to the influence on the spin Hamiltonian parameters, for example, on the magnetic shielding of nuclei by electron shells, which is predicted by the results of quantum-chemical calculations (chemical shifts).

³³ Thus, the Bruker firm reported in 2002 on the achieved productivity of one of the NMR spectrometers on a level of 1400 ¹H spectra per day.

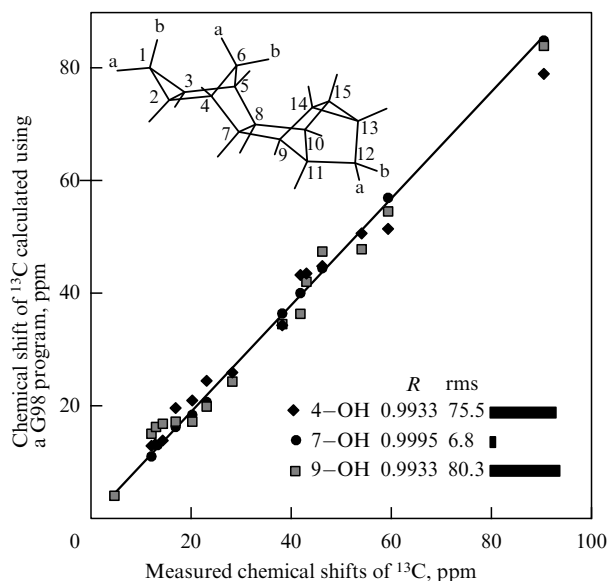


Figure 8. Demonstration of the potential of one of the modern program packets for *ab initio* calculations of the NMR CSs for ¹³C, aimed at the determination of the structure of a complex organic molecule from the class of triterpenes (the structure of the carbon skeleton is shown in the upper left-hand corner of the figure). The attributions were performed for three different positions of the hydroxyl group (see symbols in the bottom right-hand corner of the figure). The preference of the second variant (7-OH) [maximum correlation coefficient *R* and minimum root-mean-square (rms) deviation] is obvious. Data were provided by Yu A Strelenko (Institute of Organic Chemistry, Russian Academy of Sciences).

The creation of novel advanced methods for quantum-chemical calculation of the CS and ISSI, such as the GIAO DFT and CSGT DFT methods,³⁴ was a great achievement in the field of NMR application to the interpretation of molecular structures. This allowed *ab initio* calculation programs to become a commercial product and greatly facilitated the identification of complex organic structures from NMR spectra. NMR measurements of ¹³C and ¹H spectra make it possible to determine the structure of many (especially structurally rigid) organic compounds via a direct comparison of the calculated data with experimental results.

Figure 8, published by Yu A Strelenko in the Russian bulletin *Novosti YaMR v Pis'makh*,³⁵ schematically displays a structure with 15 carbon atoms, to one of which there is connected a hydroxyl group OH, and the root-mean-square (rms) deviations of experimental data from the results of calculations using a G98 *ab initio* program packet for three positions of OH. In the structure with OH at the 7th carbon atom, the rms deviations are less than those characteristic of

³⁴ The GIAO DFT (Gauge-Included Atomic Orbitals Density Functional Theory) and CSGT (Continuous Set of Gauge Transformations) methods represent a development (in the new technique of the functional-density theory) of methods of *ab initio* calculations according to Hartree, Fock, Pople, and Slater, with allowance for electron–electron correlations. These methods are successfully applied to the calculation of NMR CSs of nuclei such as ¹³C, ¹⁵N, ¹⁷O, ²⁹Si and others, including the nuclei of transition elements, and to the calculations of the EPR parameters (e.g., of free radicals). Modern approaches to the problem are considered in, e.g., Refs [177, 178].

³⁵ The bulletin *Novosti YaMR v Pis'makh* (*NMR News: Letters*) has been published by the Association of Russian NMR Spectroscopists (now in Kazan') since 1990. The materials published in the bulletin in fact represent preprints or private communications.

the two other positions by an order of magnitude. This attribution is confirmed by independent experiments.

3.3 Use of magnetic resonance for solving urgent applied problems

A spectacular example of the application of the NMR method is the recognition of the natural or technogenic origin of ethyl alcohol; the relative content of deuterium in the different groups of its molecule ($\text{CH}_3\text{CH}_2\text{OH}$) is determined not only by the initial plant product employed for its production (beet, cane, different types of grapes), but even by the site of growth of the product (see Ref. [179]). The so-called H/D isotope portraits of complex organic compounds make it possible to investigate the mechanisms of the biosynthesis of these compounds in nature. The very possibility of using this method is determined by the successes of experimental techniques, since the natural content of the ^2H isotope in the natural compounds of hydrogen is on the average 0.012% (its variations caused by isotope effects are also on the order of $\pm 0.01\%$), and the relative intensity of the ^2H NMR signal in comparison with the ^1H NMR signal is 9.65×10^{-3} .

Another example is the application of NMR spectroscopy of metabolites (urine) for the recognition of hereditary diseases (in babies) and toxicoses (in adults). The successful application of NMR for these purposes was reported by researchers at Bruker and the Center of Magnetic Spectroscopy and Tomography (CMST) of M V Lomonosov Moscow State University.

Some applications of EPR appear to be simple and are at the same time quite effective. As examples, there can be mentioned a procedure (well developed at the Bruker firm) of estimating the age of remains in archaeology proceeding from the concentration of radiation defects in the dental enamel (determining the intensity of the EPR signal), which is proportional to the integrated dose of the cosmic and background radiation since the time of the enamel formation; the quality control of beer by the EPR method, etc.

Among the most important applications of magnetic resonance is the development of quantum computing (see, e.g., the book by K A Valiev and A A Kokin [174, pp. 121–285]).

Various methods of magnetic resonance (EPR, NMR, NQR) are widely used in studies of high-temperature superconductors (HTSCs). The nature of the high-temperature superconductivity of mixed oxides, 123 compounds, and other classes of HTSCs has not yet been understood completely. Studies of HTSCs using the magnetic resonance methods, which are carried out both in the superconducting and in the normal states with the purpose of studying the structure of these compounds, help to reveal equivalent and nonequivalent positions of atoms, localized and delocalized electron spins, etc. (see, e.g., Refs [180–182]).

In the field of photochemical effects and photosynthesis upon irradiation by light, the NMR and EPR methods are utilized for observing chemical polarization of nuclear and electron spins, which makes it possible to understand the mechanisms of photochemical reactions and, in particular, details of the photosynthesis mechanisms (see, e.g., Ref. [183]). This is one of the most important directions in spin chemistry. Other photochemical effects are also being investigated, for instance, singlet–triplet transitions and annihilation of triplet states. At present, time-resolved EPR spectroscopy is widely used, which investigates transient processes with low (microsecond and sometimes even

nanosecond) characteristic times. In photoprocesses, both the transfer of the nonequilibrium polarization induced by magnetic resonance and the indirect methods of observing magnetic resonance (the above-mentioned RYDMR and MARY measurements) are also employed.

Let us now touch on four of the most promising modern applications of magnetic resonance in greater detail.

3.4 Magnetic resonance imaging in medicine

The improvement in MRI methods, which were initiated in the 1970s [184, 185], and their wide introduction into practical medicine continues at present in accordance with the title of the Nobel Lecture of Paul Lauterbur [186]: “All science is interdisciplinary—from magnetic moments to molecules to men.” Throughout the world, several thousand medical magnetic resonance (NMR) tomographs are operative; their resolution, sensitivity, and methods of contrasting images are continuously being improved. The tendency lately is the use of ever growing polarizing fields for the tomographs—from 0.5 to 4.0 and even to 7.0 T, which increases the sensitivity, shortens the time of exposure, and, as experience has shown, carries no danger for the health of patients. An increase in the polarizing field induction makes it possible to obtain an ever increasing volume of information about the state of health of patients. An important achievement in modern MRI procedures appears to be the development of methods for virtually completely eliminating the NMR response to signals from ‘uninformative’ structures (for example, the elimination of the more slowly relaxing signals of free water and adipose tissues in the brain) with the retention of information about the functionally important structures. These techniques are based on manipulation with intensities of signals by means of pulsed resonance actions and via the selection of the instant of observation of the more rapidly relaxing ‘useful’ signal, which coincides in time with the passage of the masking signals through the zero values in the process of relaxation [187, pp. 58–94]. The arsenal of MRI technologies is being enlarged continuously. This method became irreplaceable in clinical practice for diagnosing the pathologies of soft tissues.

A standard NMR tomograph gathers information about 15 sagittal sections (each on the order of 5 mm thick) of the brain of an adult. Each section contains information about 256×256 unit volumes (so-called pixels or voxels). Already the very fact of whether each voxel gives an ^1H NMR signal or not contains approximately 20 information units (bits). However, this is only information concerning the volume occupied by the vitally important parts of the brain; each voxel which contains the image of a group of living cells gives a signal whose intensity depends not only on the dynamics and structure of the environment of protons in the organism, but also on the conditions for excitation and detection of NMR signals.

Figure 9 displays a tomogram [sagittal section, which was kindly supplied to us by V N Anisimov (MSU CMST)] of the brain of a clinically healthy patient.

To facilitate the ‘reading’ of the tomogram of the brain by a specialist-physician, the intensity of the signal is sometimes coded in the regime of ‘a million colors.’ Thus, the above-indicated packet of tomograms contains at least 40 bits of information. Without pretending to the correct estimation of the ‘usefulness’ of available information, note that its large volume became accessible only because of the high spatial

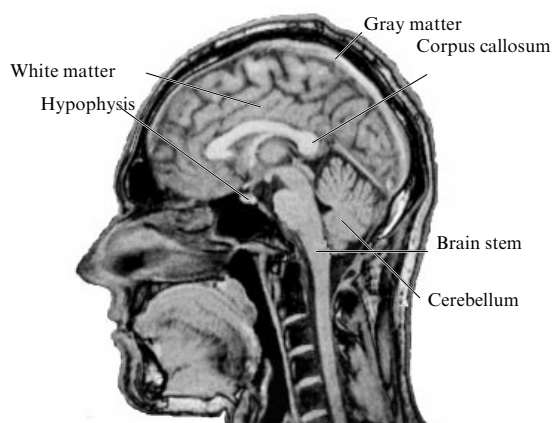


Figure 9. Sagittal section of a magnetic resonance image of a practically healthy patient. The image was obtained at the Center of Magnetic Spectroscopy and Tomography, Moscow State University, by N V Anisimov.

resolution and high ratio of the NMR signal to noise. A valuable property of NMR tomography is the possibility of using different methods to diversify signals from different sections of the object investigated. If we turn to the Bloch equations (this approximation is suitable for describing similar experiments), we see that the intensity of the signal of each voxel i is determined (a) by the number n_i of spins in a given volume, i.e., by the magnetic moment M_i of this volume, and (b) by the times of longitudinal (T_{1i}) and transverse (T_{2i}) relaxation of the magnetic moment of the predominant phase (structure) of a given volume.

Special methods of preparing an object also exist, for example: (a) the introduction into the tissues of a special 'spin probe'—xenon; (b) the introduction of a special paramagnetic reagent (for instance, a gadolinium salt) which affects the rate of relaxation (a contrasting agent), and, finally, (c) the above-mentioned trick of using, for the observation, only part of the spins of the volume investigated, which either have specific values of T_{1i} or T_{2i} , or specific values of the CS of the NMR frequency. It should be also noted that the so-called useful information becomes truly useful if the tomograms of the brain and other organs are examined by a trained physician, a specialist with much practical experience, who knows much about the structure, functions, and disfunctions of these organs. A successful interpretation of modern medical tomograms is possible both owing to the long distance covered by biology and by clinical medicine and due to an unprecedented growth in the sensitivity, resolution (which was mentioned above), and many systematic improvements of pulsed NMR methods.

3.5 Methods of magnetic resonance in modern natural science. Nuclear magnetic resonance of proteins

Magnetic resonance methods have played an important role in the gradual solution of a significant and complex problem in biochemistry—the study of the structure and dynamics of protein macromolecules (proteins). The nuclear magnetic resonance of proteins is usually investigated in aqueous solutions, using specimens containing from 300 to 600 μl of solution with the concentration of 0.1–3 millimoles

of a protein. The specimen can be both natural and extracted from a biological system that contains a recombinant DNA created with the aid of gene engineering.³⁶ The NMR of proteins obtained from natural sources is limited to the use of exclusively PMR (^1H NMR). However, NMR of the low-abundance isotopes ^{13}C and ^{15}N gives unique information about the structure and dynamics of a protein chain.

The proteins enriched in ^{13}C and ^{15}N isotopes, which are released by microorganisms with a recombinant DNA, offer possibilities of conducting more informative multivariate experiments. The isotope enrichment is performed by growing a bacterial or fungus culture on a growth medium which contains the necessary isotope. The isotopically enriched compounds are expensive, and for these experiments organisms that can grow on 'basal' media containing only one source of ^{13}C isotopes, such as glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (most frequently), sometimes glycerin $\text{C}_3\text{H}_5(\text{OH})_3$ or methanol CH_3OH , or such sources of ^{15}N isotopes as ammonium chloride NH_4Cl or ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, are chosen. The most frequently used genetically engineered organisms are bacteria, such as the *Escherichia coli* (colibacillus) and yeast fungi, for example, *Saccharomyces cerevisiae*. Such genetically modified lower organisms synthesize proteins characteristic of higher organisms and allow the isotopic enrichment of ferments, proteins, and other biologically active compounds of higher organisms.

The methodology of the NMR studies of biopolymers has travelled a great way to reach biologists and biochemists. Not only two-dimensional (2D), but also three-dimensional and four-dimensional³⁷ (3D and 4D) methods of representing information have been developed. The basic steps along this path are reflected in the review by L Kay [188] and in a review by V I Pol'shakov published in the Russian bulletin *Novosti YaMR v Pis'makh (NMR News: Letters)* (see above, footnote 35). These steps are as follows.

(1) The main laws that govern the magnitudes of ISSIs between nuclei depending on the angles between the chemical bonds (configuration of the polymer chain) are developed—R Karplus, V F Bystrov and others (1950s–1970s).

(2) Two-dimensional NMR spectroscopy is developed—R Ernst, K Wüthrich and others (1970s–1980s).

(3) The separation of signals of rapidly and slowly diffusing molecules is achieved under the influence of the pulsed gradient of a magnetic field—D W McCall, E O Stejskal and others [116], R Hurd [189] and others (1990s).

(4) Measurement and calculation methods of residual DDIs for the orientation of protein molecules in lyotropic (liquid-crystal) oriented media suitable for evaluating mutual orientations of chemical bonds are developed—J H Prestegard and others [190] (1996).

(5) A selective narrowing of lines in the NMR spectrum of nuclei with an anisotropic chemical shift and DDIs is obtained when strengthening the polarizing field (in the two-

³⁶ The desired parts of the DNA of higher organisms are built into the DNAs of lower organisms, which can be grown on artificial media.

³⁷ A three-dimensional (four-dimensional) design of the presentation of NMR data is ensured by the variation of, correspondingly, two (three) intervals of time between the pulses in the complex multipulse experiment. The last measurement (frequency of the observed resonance) is always ensured by the variation in the time of taking-off of the data at the end of the experiment. As the third coordinate, the time of the 'thermal contact' between unlike spins can be utilized.

dimensional modification of TROSY)³⁸ — K Pervushin, K Wüthrich and others [191] (1997).

(6) A method for measuring the relaxation of deuterium nuclei in side polymer chains for evaluating their mobility is developed — L Kay, V Tugarinov and others [188] (2002).

The first two steps made it possible at the then level of sensitivity to produce in the solution (with the application of NMR) structures of amino-acid chains with up to 20–30 links. Progress in the potential of NMR for the establishment of protein structure, which is evinced by the growth of the dimensions (number of amino-acid links) of proteins accessible for interpretation, has been demonstrated in Ref. [188]. In the 1980s, there were accessible systems with 73 amino-acid links (for example, the so-called ubiquitin). In recent years, the identification of the structure of the amino-acid chains of the enzyme malate synthase G (MSG) with 723 links has become possible (V Tugarinov, L Kay and others [188]). Certainly, for determining such structures, in addition to NMR data, the results of molecular dynamics calculations and a comparison of the data for liquids with X-ray diffraction measurements in crystals (where this is possible) are used.

The integration of all areas and methods of contemporary natural science can hardly be expressed more obviously than in the comparatively new scientific discipline—proteomics—connected with studies into the structure and dynamics of proteins.

3.6 Application of dynamic polarization of nuclei in biochemistry

Among the newest achievements of magnetic resonance methods, we should note the use, in biochemical studies, of dynamic nuclear polarization (DNP) based on the saturation of the EPR of free radicals, paramagnetic ions, or biradicals admixed into a frozen solution cooled to a temperature of 1.2 K (cf. Ref. [148] and Section 2.9). A detailed and very inventive prescription for the preparation of a specimen with 25–40% polarization of the ¹³C and ¹⁵N nuclei was described in Ref. [192]. The specimen is dissolved in boiling water and then is moved mechanically into a high-resolution NMR spectrometer. There, in spite of a 6–8-second delay, the signals of the nuclei still exceed the thermally equilibrium value by 10⁴ times.

When our article had already been prepared for publication, a special issue of the journal *Applied Magnetic Resonance* appeared [193], which was completely devoted to the theory and experimental realization of this surprising method. For example, a cyclic unfreezing (by a pulse of an IR laser) and freezing of a specimen is accompanied by repeated acts of DNP at a temperature of liquid-nitrogen vapors and by the usual detections of two-dimensional high-resolution NMR in the unfrozen solution.

3.7 Magnetic-resonance force microscopy and the ultimate sensitivity of magnetic resonance methods

Magnetic-resonance force microscopy (MRFM) [194] serves as one of the modern methods of magnetic resonance. The first attempt to apply the mechanical method of registering the gyromagnetic effect was an experiment devoted to the Einstein–de Haas effect, described in detail in book [31, Chapter 4]. A variant of

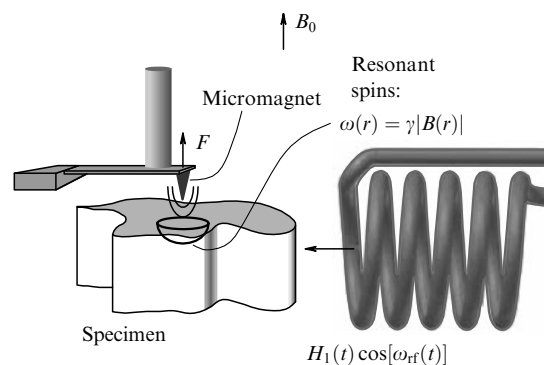


Figure 10. A schematic of the magnetic-resonance force microscope (MRFM). Shown are a fixed lever (loaded with a mass m) with a spring constant k , a micromagnet with an induction gradient ∇B , and a resonance coil (borrowed from review [194]).

the mechanical recording of magnetic resonance was mentioned in Ref. [23, p. 14].

The principle of operation of an MRFM is based on registering the deflection of a fixed thin elastic lever (cantilever) with a micromagnet (several fractions of a micron in size) upon its interaction with the spin system of a local region of the specimen to be investigated. A periodic change in the longitudinal magnetic moment of the spin system with a natural frequency ν_{mr} of vibrations of the mechanical microresonator causes vibrations of this mechanical resonator—a cantilever with a spring constant k and an effective mass m (Fig. 10).

The natural frequency of the resonator ($\nu_{\text{mr}} \approx 10^3 - 10^4$ Hz) is much less than the Larmor frequency ($\nu_{\text{mr}} \ll \nu_L \approx 10^8$ Hz for NMR or even higher for EPR and FMR). The fundamental difference between MRFM and induction methods of magnetic resonance is that the MRFM detects changes in the longitudinal (rather than transverse) component of the magnetic moment of spins. A high spatial resolution in the MRFM is reached owing to the high spatial inhomogeneity of the micromagnet's field ($\nabla B \approx 10^6$ T m⁻¹), and a high sensitivity is reached due to the high quality of the resonator ($Q_{\text{mech}} \geq 10^5$) and the application of a laser interferometer for registering oscillations of the resonator. The displacement of the resonator above the surface makes it possible for the device to function as a magnetic-resonance introscope, and the scanning and tuning of the excitation frequency allows it to function as a magnetic-resonance spectroscope.

The theory of MRFM (see, e.g., Refs [194, 195]) takes into account all the achievements of the modern theory of physical experiment [196] and predicts the possibility of realizing an ultimate sensitivity, i.e., the detection of a single spin, in particular, upon excitation of EPR [194, 195].³⁹ These predictions are close to the realization.

In this connection, let us dwell on the comparison of the sensitivity of the equipment based on the three most universal methods of registering magnetic resonance: induction [13, 14], SQUID [117], and MRFM [194]. The general expression for the signal-to-noise ratio for N_s spins I with a gyromag-

³⁸ TROSY is Transverse Relaxation Ordered Spectroscopy.

³⁹ The Russian-language translation of monograph [195] is prepared for publication.

netic ratio γ in a magnetic field H in these methods takes the form

$$\frac{S}{N} = N_s \frac{\hbar\gamma H \langle I^2 \rangle}{\sqrt{\delta\nu}} F_{\text{app}}, \quad (3.1)$$

where $\delta\nu$ is the natural width of the contour of the resonance line, and F_{app} is the instrument function of the corresponding method. A comparison of the instrument functions gives

— for MRFM:

$$F_{\text{app}} = |\nabla B| \sqrt{\frac{Q_{\text{mech}}}{4k_B T \sqrt{km}}}; \quad (3.2)$$

— for SQUID:

$$F_{\text{app}} = \sqrt{\frac{\eta V_s}{\mu_0 \varepsilon_{\text{SQ}}^e}}, \quad (3.3)$$

where $\varepsilon_{\text{SQ}}^e \sim 10^{-30} \text{ J Hz}^{-1}$ is the energy sensitivity of the quantum interferometer, and

— for the induction method:

$$F_{\text{app}} = \sqrt{\frac{\mu_0 Q_{\text{EM}} \omega_0 \eta V_s}{2k_B T}} = \sqrt{\frac{\mu_0 Q_{\text{EM}} \gamma H \eta V_s}{2k_B T}}. \quad (3.4)$$

Here, η is the filling factor of the working volume V_s of the device. The higher values of Q_{mech} in comparison with Q_{EM} and the absence of the factor $\eta < 1$ in the formula for MRFM give an obvious advantage in sensitivity to the MRFM method in a wide range of frequencies.

4. Conclusions. Some prospects

We have tried to show the generality of the historical roots and methodological principles of different branches of magnetic resonance and their close connection with the achievements of technology and natural science on the whole. After the vague guesses about the nature of magnetism in the late 19th to early 20th centuries, physics arrived at the discoveries and theoretical explanations of spin effects, including the magnetic resonance effects. Magnetic resonance became the basis of a complex of research methods in the physics of spin systems and of a complex of applied methods in quite various fields. To become better acquainted with separate problems of magnetic resonance, we send the reader to the above-cited articles, reviews, and monographs, and also to numerous review papers in *Uspekhi Fizicheskikh Nauk (Phys. Usp.)*, which we have not cited here.

The magnetic resonance methods shown their capability ‘to mature’ at that instant of time when there appears a vital need for them. They continue improving, and the ways of this improvement either have already become clear or are only planned. Let us recall the principal ones.

An increase in the strength (induction) of the polarizing magnetic field for the majority of methods remains a promising avenue for increasing sensitivity and resolution (informativeness). The induction of superconducting solenoids has reached values on the order of 25 T in NMR, and on the order of 30–40 T in EPR. In medical NMR intrascopy (MR imaging), the field strength is increased cautiously (so

far only to 7.5 T), because of considerations of patient safety. The constraints on the magnitude of the attainable induction in the superconducting solenoid are mainly associated with the finite values of the critical magnetic field for the superconductors employed in the solenoids and, to a certain degree, with the engineering solutions which ensure the minimization of the stray field outside the solenoid and of the field inhomogeneities in the volume of a specimen. There is no doubt that here a significant potential for progress exists. At the same time, in strong fields it is necessary to take into account the orientation of anisotropic diamagnetic and paramagnetic molecules by the field, which influences the measurements of ISSIs and CSs [197].

The second and the main potential for the development of magnetic resonance methods is related to the improvement of the procedures of excitation and detection of signals. The selection of special procedures for each class of objects and tasks of a study, based on the unique possibility of experimental manipulation with the parameters of a spin Hamiltonian (‘spin choreography’ and ‘spin alchemy’) was always the basis of new successes in the application of magnetic resonances in spectroscopy and magnetic tomography. Most frequently, this reduces to an appropriate selection of pulse sequences for the excitation of signals of free induction of the transverse component of magnetic moments. The use and pulsed regulation of high gradients of the polarizing field, as well as obtaining signals during the modulation of the longitudinal rather than transverse component of the magnetic moment (as in MRFM), give additional possibilities.

Let us also point to some methods for improving equipment that are essentially known, but practically far from being exhausted. These are the application of cryoprobes and SQUIDS, the use of mechanical and optical methods of signal detection, an increase in the rate of rotation of solid-state specimens, and, finally, the use of ‘multipass’ methods of preparing specimens, such as freezing with an addition of free radicals, dynamic nuclear polarization with saturation of EPR, and the transfer of polarized nuclei after unfreezing to a high-resolution NMR spectrometer [193]. New possibilities are also expected in the studies of spin-controlled processes in extremely high or low magnetic fields due to a special selection of subjects and the original design of experiments.

There are also a number of incompletely solved problems in the theory. Up to now, no wide application has been found for the generalized theory of the line shape for arbitrary spin systems [175]. Among the most important problems of magnetic-resonance molecular spectroscopy, we can mention the further development of the quantum-mechanical theory of the spin Hamiltonian parameters (see, e.g., Ref. [178]). How wide and diverse the problems that can be solved with the aid of magnetic resonances are, one can judge from the Appendix, in which we enumerated the Nobel Prize Laureates for achievements in the fields connected with magnetic resonance.

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5. Appendix

Nobel Prize Laureates for achievements in the field of magnetic resonance

No.	Subject	Year	Achievements (<i>notes</i>)	Laureate
1	Physics	1902	“in recognition of the extraordinary service they rendered by their research into the influence of magnetism upon radiation phenomena” (<i>discovery of the Zeeman effect</i>)	H A Lorentz, P Zeeman
2	Physics	1943	“for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton” (<i>discovery of quantization of projections of the magnetic moment of the proton</i>)	O Stern
3	Physics	1944	“for his resonance method for recording the magnetic properties of atomic nuclei” (<i>observation of nuclear magnetic resonance in molecular beams</i>)	I I Rabi
4	Physics	1952	“for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith” (<i>observation of nuclear magnetic resonance in matter</i>)	F Bloch, E M Purcell
5	Physics	1966	“for the discovery and development of optical methods for studying Hertzian resonances in atoms” (<i>double optical paramagnetic resonance</i>)	A Kastler
6	Physics	1977	“for their theoretical investigations of the electronic structure of magnetic and disordered systems”	J H van Vleck (jointly with P W Anderson and Sir N F Mott)
7	Physics	1989	“for the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks” (<i>hydrogen maser of hyperfine atomic levels</i>)	N F Ramsey (one half of the prize)
8	Chemistry	1991	“for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy” (<i>for the pulsed methods of high-resolution nuclear magnetic resonance</i>)	R R Ernst
9	Chemistry	1998	“for his development of computational methods in quantum chemistry” (<i>including the parameters of spin Hamiltonians</i>)	J A Pople (one half of the prize)
10	Chemistry	2002	“for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution” (<i>determining protein structures</i>)	K Wüthrich (one half of the prize)
11	Physiology or Medicine	2003	“for their discoveries concerning magnetic resonance imaging”	P C Lauterbur, Sir P Mansfield

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