

Chapter 2

Basic Principles of Detection of Nuclear Magnetic Resonance

As we might expect, for the observation of NMR it is required permanent magnetic field $\vec{B}_0$, in which the Zeeman splitting of energy levels of the spin system is realized, and a alternating radio frequency field $\vec{B}_1$, stimulating transitions between the Zeeman sublevels. As a consequence of this interaction the spin system can emit or absorb the energy of the RF field, if the frequency of the field (ν) is close to the frequency of transitions (ν_0). Thus, for the observation of the nuclear magnetic resonance it is necessary to have the following main instruments: (i) sources of static and alternating magnetic fields, (ii) a device that converts the energy of the quantum transitions in the RF signals, (iii) amplifiers and hardware for registration of these signals.

Observation of NMR can be performed during continuous irradiation of alternating magnetic field $\vec{B}_1$, well as between its pulses. In this regard, the principles of observation NMR in condensed media are divided into two groups, differing from each other both experimental methods and classes of solved tasks. In the first years after its discovery the nuclear magnetic resonance observed mainly with stationary RF exposure field $\vec{B}_1$, but soon the technique of its observations in the presence of pulsed RF field $\vec{B}_1$ was developed. Until the 70-ties, both techniques developed in parallels, solving the characteristic for their class specific tasks (the study of spectra on the basis of a stationary radiation field $\vec{B}_1$ and relaxation processes by pulsed irradiation). The development of experimental technologies and the emergence of powerful and high-speed PC led to the formation of the Fourier transform NMR spectroscopy, which united both directions.

2.1 Nuclear Magnetic Resonance in Molecular and Atomic Beams

The phenomenon of nuclear magnetic resonance for the first time was observed by I. Rabi and co-workers (1938), in experiments with atomic beams. By this time, experiments of O. Stern and W. Gerlach were already well known, which allowed to

estimate the magnetic moment of an atom, as well as works I. Estermann, O. Stern, and R. Frisch to determine the proton magnetic moment. All of them used the fact, that in an inhomogeneous magnetic field a particle, which has a magnetic moment ($\vec{\mu}$), is subjected by the force (see the details in Sect. 18.1)

$$\vec{F} = \mu_z \frac{\partial \vec{B}}{\partial z}, \quad (2.1)$$

where $\frac{\partial \vec{B}}{\partial z}$ is the magnetic field gradient; μ_z is the component of the magnetic moment directed along the axis z . Under the influence of ($\vec{F}$) the particle will be deflected in the direction of the axis z . The magnitude of this deviation (dz) will be determined by the kinetic energy of the particle (E), its magnetic moment ($\vec{\mu}$) and magnetic field gradient:

$$dz = \vec{F} \frac{A}{E} = \mu_z \frac{\partial \vec{B}}{\partial z} \frac{A}{E} \quad (2.2)$$

(A is a constant depending on the geometric parameters of the device).

Knowing instrument parameters, the value of $\frac{\partial \vec{B}}{\partial z}$ and the average kinetic energy of particles in a beam, as seen from (2.1), one can define μ_z from the value of dz . However, even in the most advanced experiments of I. Estermann and O. Stern, the accuracy of the measurements of magnetic moments was not high: for the proton not better than 10%. For determining the magnetic moment of microparticles by the Rabi method, on a certain part of the particle trajectory the conditions for magnetic resonance is created. The interaction of nuclear (or electronic) magnetic dipole with alternating field has been brought to its reorientation. The method consists in the following. The low-pressure chamber O (Fig. 2.1a) ($P \simeq 10^{-6}$ mm Hg $\simeq 10^{-8}$ Pa) creates a beam of particles (atoms or molecules) which trajectories sequentially pass through the gaps of magnets A and B. These magnets are identical: inhomogeneous magnetic field in their gaps is equal in magnitude $|B_A| = |B_B|$, but with opposite direction of the vectors of field gradients, and $|\partial B / \partial z| \simeq 800$ T/m. In this regard, the particle, flying through the gaps between magnets A and B, will be subjected to the same deflection, first, in one direction and then in the opposite direction and get on sensor detector D (Fig. 2.1b).

If the investigated particles are molecules with compensated electron spins (molecules of $^1\Sigma_0$ -state) or atoms then the magnetic properties of these particles and their interaction with external magnetic fields are determined only by moments of the nuclei. Between the magnets A and B there is the magnet C, in which gap a highly-homogeneous magnetic field $\vec{B}_0$ is created. In addition, in the magnet gap the loop L of length l is set, which created an alternating magnetic field $\vec{B}_1(t)$, and which oriented perpendicular to the field $\vec{B}_0$. The principle of operation of the loop is illustrated in Figs. 2.1b and 2.2a.

As a result of effect of the static $\vec{B}_0$ and alternating $\vec{B}_1$ magnetic fields on magnetic dipole $\vec{\mu}$, this dipole will be re-oriented (see Sect. 1.2). The length of the loop l and

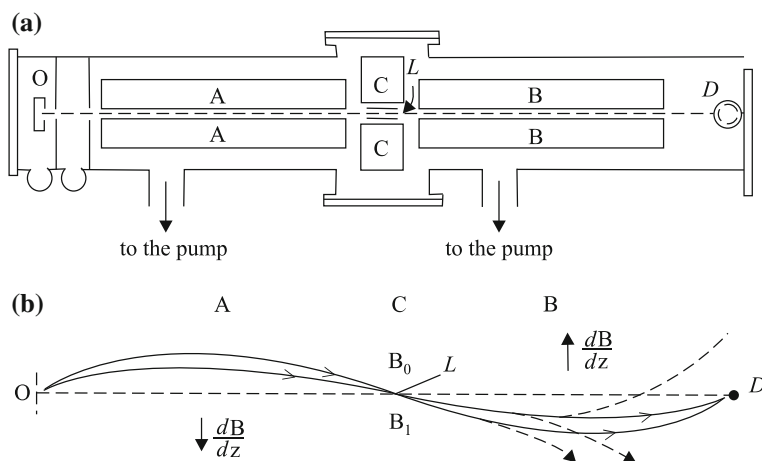


Fig. 2.1 The functional diagram of the detection of NMR by Rabi method

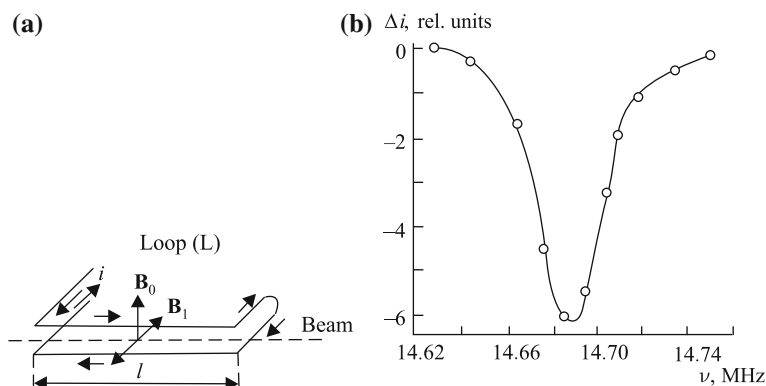


Fig. 2.2 **a** The scheme of a loop for creating of the alternating magnetic field; **b** The resonance curve of ^1H nuclei in the beam of the KOH molecules

the field strength B_1 is matched so, that for the span time (t) of particles through the magnet gap, all the dipoles $\vec{\mu}$ were reoriented (sign μ_z is changed to the opposite one). Therefore, in accordance with (2.1), in the magnet gap B they will be deflected in the same direction as in the magnet gap A, and will not reach the detector D. Since the intensity of the reorientation process of magnetic dipoles increases with the frequency detuning ($\Delta\nu = \nu_0 - \nu$) decrease, then the flow particles falling into the slot of detector D must decrease. Consequently, the current i in the detector circuit will change simultaneously with the change $\Delta\nu$. This change of $i(\Delta\nu)$ has a resonant character. As an example, Fig. 2.2b shows the NMR signal from nuclei ^1H in the beam of the KOH molecules, obtained in the $B_0 = 0.3453$ T.

The observed resonance lines in such a way allow us to determine the frequency and line width, to investigate the shape of the signal and other characteristics of the spectrum of nuclear magnetic resonance in atomic and molecular beams.

If one studies hydrogen molecules, the NMR signal is observed only from the ortho-hydrogen (which possesses the total nuclear spin $I = 1$). In molecules of parahydrogen ($I = 0$) spins and magnetic moments of the proton pair are antiparallel, and the reorientation of the magnetic dipoles of individual protons in the magnet C does not change the magnetic properties of the molecule as a whole and the trajectory of its movement.

Using NMR on beams, gyromagnetic ratios and magnetic moments of many nuclei were measured with greater accuracy than it was done previously by other techniques.

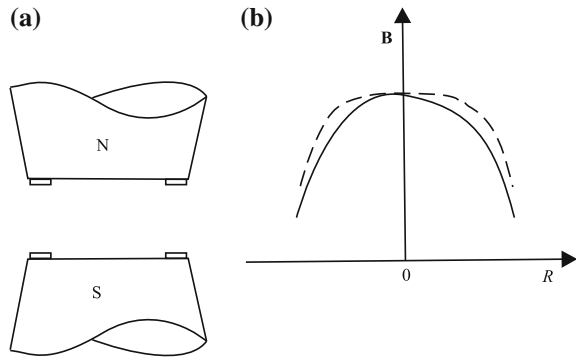
2.2 The Sources of Magnetic Fields

The range of used fields values is approximately 0–20 T. As a rule in the region 0.1–2 T electromagnets or permanent magnets are used and fields with the induction of more than 2 T for the nuclear magnetic resonance can be obtained only in solenoids with a superconductive winding coil. At low fields (less than 0.1 T) one uses conventional solenoids or even Earth magnetic field (0.00005 T).

The main requirements to the static magnetic field are (i) sufficiently high homogeneity within the scope of an investigated sample and (ii) field stability over time. The value of the average deviation of the field ΔB within a sample divided to the magnitude of the resonance field B_0 is taken as a measure of the field homogeneity. For measurements of relaxation times and self-diffusion coefficient in many cases it is sufficient to achieve the value $\Delta B/B_0$ of order of 10^{-5} to 10^{-6} , but to obtain high resolution NMR spectra a value $\Delta B/B_0$ is required not worse than 10^{-8} to 10^{-10} . A high degree of homogeneity in the gap of an electro- or permanent magnet can only be achieved through the set of design measures to gradually increasing the field homogeneity. The yoke of magnet is usually of H-shaped form that provides sufficient rigidity and symmetry of design in conditions of significant static compression loads between the poles (mutual force attraction of the pole pieces may be several tons).

To reduce edge effects (decreasing of the induction between poles at the edges of a gap relative to the center), the diameter of the pole pieces (D) is chosen much larger than the gap between poles (d): $D/d \geq 10$. With the same aim one can use the so-called *shimming*—a decrease of the d at the periphery of the gap by introducing additional annular rings (Fig. 2.3a). By special design of the rings it is possible to expand significantly the volume of homogeneous field (see in Fig. 2.3b, dashed curve). The shimming efficiency drops rapidly with an increase of the level of B_0 due to saturation of iron at $B_0 > 1$ T and in this connection this type of shimming is almost never used in modern instruments.

Fig. 2.3 The influence of the shimming on the magnetic field in a magnetic gap



Pole pieces are made using soft (without carbon impurities) iron, followed by a thorough multi-stage machining, polishing and annealing in hydrogen atmosphere. As a result of processing, mechanical irregularities do not exceed $0.25 \mu\text{m}$. Parallelism of surfaces of the pole pieces also significantly effects on the resulting homogeneity. Thus, the deviation from parallelism in $2\text{--}3 \mu\text{m}$ at $D \simeq 30 \text{ cm}$ leads to inhomogeneity $\Delta B/B_0 \simeq 10^{-6}$. Careful adjustment of poles with control by NMR signal allows us to obtain $\Delta B/B_0 \simeq 10^{-7}$. The next step towards improving the field uniformity is the compensation of inhomogeneities using the current-carrying conductors—*current shims*.

The magnetic field in a certain volume, which has no sources, can be described analytically using the scalar potential Φ , satisfying the Laplace equation $\nabla^2 \Phi = 0$. Then the field in this volume is $\vec{B} = -\vec{\nabla} \Phi$. The potential Φ can be represented as a series of three-dimensional spherical harmonics:

$$\Phi = \sum_{n=1}^{\infty} \sum_{m=0}^n r^n P_n^m(\cos \theta) [A_n^m \sin m\varphi + B_n^m \cos m\varphi].$$

Here $P_n^m(\cos \theta)$ is the adjoint Legendre polynomial. Coefficients A_n^m and B_n^m do not depend on coordinates and are completely determined by the sources of the field. The terms with $n = 1$ describe three components of the field (uniform field), with $n = 2$ —field gradients. The problem is in the design of current loops which magnetic fields will reproduce separately each harmonic of the general expansion of the field. To compensate the inhomogeneity we need to choose the electric current in the loops so that their magnetic fields will be equal in magnitude to the corresponding harmonics and opposite in sign. It is easy to achieve experimentally, setting sequentially in each compensator such a current at which the highest resolution is obtained for the NMR spectrum. A sample should fill that volume, in which the used spatial harmonics form a closed and orthogonal system of functions, i.e. for a spherical sample centered at the origin are suitable spherical harmonics.

Due to the mutual orthogonality of spherical harmonics the configuration of the field created by one of the compensators, can not be obtained through any combination of fields of all other compensators, so the current value in each of the compensators, corresponding to the best uniformity, does not depend on currents in other compensators. Strictly speaking, the orthogonality holds only for a spherical sample centered at the origin. However, almost independent adjustment is saved for other configurations (for example, cylindrical ones), but not too elongated or flattened. In order to achieve full compensation, in principle, it is necessary to create an infinite number of harmonics, but the contribution of higher harmonics is small, thus one uses components with $n = 2, 3, 4$.

In calculations of the current configuration it can be assumed, that the component of the field, which is tangential to the surface, is perpendicular to the vector current density surface, i.e. current vector is directed along the lines of equal potential: $\Phi = \text{const}$. Obtained configuration of conductors for planar surfaces of electromagnet pole pieces are complex and is not practically feasible to manufacture.

B. Anderson (1960) proposed a simpler system of currents based on expansion of the field in the series:

$$B_{0z} = B_0 + \left(\frac{dB_z}{dx}\right)x + \left(\frac{dB_z}{dy}\right)y + \left(\frac{dB_z}{dz}\right)z + \dots \quad (2.3)$$

Here, the first derivatives with respect to three coordinates are linear field gradients. Although it is an infinite power series, only a small number of gradients is practically significant. For a rough compensation three linear and three quadratic derivatives can be used. Linear gradient is easily obtained using a system of two parallel conductors with a current. As can be seen from Fig. 2.4a, two long conductors with equal currents create at the axis R a linearly varying field. The real configuration of the conductors, located on each of the planes pole pieces, is shown in Fig. 2.4b. Since the system antisymmetric, then the expansion (2.3) contains only odd powers decomposition. Variables h_1 and h_2 can be chosen so, that factor with third-degree expansions were equal to zero. Then the first noncompensated coefficient would be only one of the fifth degree, the value of which is negligible. The calculation gives the following relationship:

$$h_{1,2} = (3 \mp 2\sqrt{2})\delta.$$

(δ is the distance between the planes, where conductors are placed).

The system, shown in Fig. 2.4b, creates a gradient $d\vec{B}_{0z}/dx$. It is obvious, that for the formation of the gradient $d\vec{B}_{0z}/dy$, we can use a similar system, but turned on 90° around the axis z . To create the gradient $d\vec{B}_{0z}/dz$ it is more convenient to use two rings with opposite direction of current (see Fig. 2.4c). The optimum ratio between the radius of the ring R and value δ is given by

$$R = \frac{2}{\sqrt{3}}\delta.$$

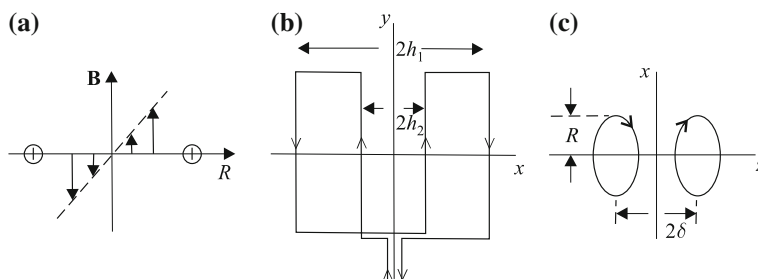


Fig. 2.4 The principles of creating of the field gradients. **a** The creating of the field gradient by two linear conductors. **b** The practical scheme for creating the field gradient $d\vec{B}_{0z}/dx$. **c** The scheme of two rings for creating the field gradient $d\vec{B}_{0z}/dz$

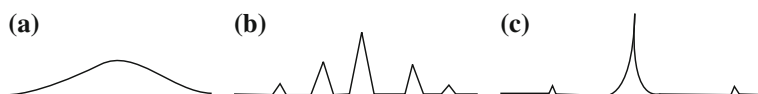


Fig. 2.5 The effect of sample rotation on a spectral line

Similarly the gradients of higher orders are formed.

The system of the current compensator allows us to improve the homogeneity, at least an order of magnitude (roughly to 5×10^{-8}). Further improvement of the homogeneity is achieved by spinning of a sample. If the magnitude of inhomogeneity in the sample volume is ΔB , the rotation of an ampoule with a sample averages the inhomogeneity of field to some effective value:

$$\Delta B_{\text{eff}} = \gamma \langle (\Delta B)^2 \rangle \tau,$$

where $\langle (\Delta B)^2 \rangle$ is the standard deviation of the field within a sample, τ is the averaging time (time of one revolution of an ampoule). The rotation of an ampoule performed by means of a gas turbine with compressed the air. The frequency of rotation is chosen sufficiently high (up to 300 Hz) in order to reduce the value of ΔB_{eff} . In addition, rotation of a sample at low frequencies leads to satellites in a spectrum—additional signals located symmetrically with respect to the main ones (Fig. 2.5a, b). The increase of rotation speed reduces them and moves beyond the recorded range of the spectrum (Fig. 2.5c).

Requirements to the stability of the field strength must be matched with degree of homogeneity, at least for the time needed for the NMR signal registration. Stabilization of the field $\vec{B}_0$, generated by electromagnets or coils, is usually provided by a multi-stage system containing an electronic current stabilizer, stabilizer of induction flux in the magnet gap and stabilizer of the resonance conditions on the basis of the NMR phenomenon (lock-stabilization). In the superconducting solenoids required stability is ensured without any additional hardware, only by lock.

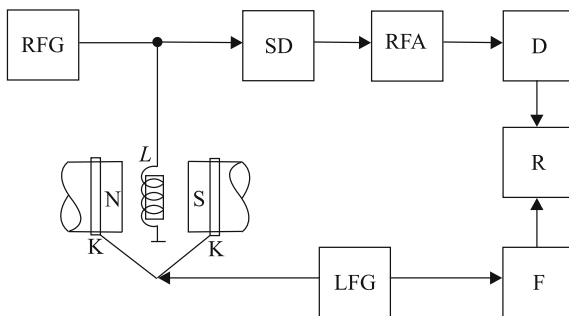


Fig. 2.6 The simplest block-scheme for the NMR observation by the stationary method

2.3 The Stationary Methods of Observation of Nuclear Magnetic Resonance

Let us first consider the basic principles of the NMR observation using stationary radiofrequency field $\vec{B}_1$. Now these methods are used in NMR in very rare cases but they are usual in EPR. So, it is reasonable to consider them in historical and methodological aspects.

The simplest functional diagram for the observation of NMR signals is shown in Fig. 2.6. The coil (L) with the investigated sample is placed in the gap of a magnet or other source of a static magnetic field $\vec{B}_0$ and oriented so that its axis and, hence, the vector of the alternating field $\vec{B}_1$ are perpendicular to the direction of the field vector $\vec{B}_0$. The radiofrequency field $\vec{B}_1$ is created in the coil L connected to the radio frequency generator (RFG). In order to perform periodic observation of the NMR the static magnetic field is modulated by additional coils (K), connected to a generator of sinusoidal or sawtooth voltage of low frequency (LFG). The horizontal sweep signal on the oscilloscope screen is realized also with the LFG. Since the NMR signal reaches a maximum twice for a period of a sine sweep, then in this case to coincide the two signals in the screen an adjustable link phase shifter (F) may be used.

The main part of the device is a spin detector (SD), which converts the energy of the quantum transitions between Zeeman sublevels in the radio frequency signals. A variety of devices containing resonant circuits (RF bridge, RF-generator of weak oscillations, superregenerator and etc.) is used as a spin detector. Obtaining in a spin detector RF signals are amplified (RFA), detected (D), and fed to the registration device (R) (oscilloscope, computer, etc.). There are four main elements of the scheme: (1) a spin detector; (2) a source of the magnetic field $\vec{B}_0$; (3) a system of amplification, detection, and registration; (4) a system for passing through the resonance (modulation of the field $\vec{B}_0$).

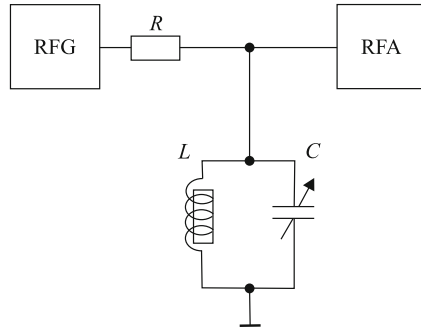


Fig. 2.7 The functional scheme of the spin detector of Rollin

2.3.1 Spin Detector

This term will denote a certain electrical circuit in which there are signals due to the precession of the vector macroscopic nuclear magnetization ($\vec{M}$). In the most cases, the basis of such a scheme is the coil (L), included in the resonant circuit tuned to the precession frequency of the $\omega_0 = \gamma B_0$. The simplest scheme of the spin detector was used by B. Rollin (see Fig. 2.7).

The RF generator with a frequency ω is connected to the parallel circuit LC , in the coil of which a sample is placed, through the ballast resistor R . The value of R is much larger than the resonant resistance of the LC circuit Z_0 , so there is a mode of current generator (current, consumed from the RFG, does not depend on Z_0). We know that under NMR conditions the maximum absorption of the RF energy in a spin system takes place. The energy loss in the resonant circuit caused by this absorption leads to a decrease of quality factor Q of LC -circuit, hence to decrease of its total resistance Z_0 and, respectively, the RF voltage on it falls. In fact, this scheme is similar to the well-known in radio engineering circuit of a Q-factor meter. If, in addition, periodically to realize the resonance condition $\omega = \omega_0 = \gamma B_0$, modulating, for example, the magnetic field B_0 , then RF voltage on the LC -circuit will be modulated in its amplitude. After appropriate amplification and detection the signal of nuclear resonance absorption can be observed on an oscilloscope screen or another registrator.

Let us obtain the formula for the quantitative estimates of this phenomenon. The conductivity of a parallel circuit (Y) is the sum of the conductivities of its branches:

$$Y = \frac{1}{R} + i\left(\omega C - \frac{1}{\omega L}\right). \quad (2.4)$$

The rotating component of the nuclear magnetization ($M_{\perp} = (M_x^2 + M_y^2)^{\frac{1}{2}}$) generates in the coil the additional magnetic flux (Φ_{add}):

$$\Phi_{\text{add}} = \xi B_1 S = \xi \cdot 4\pi M_{\perp} S = 4\pi \chi \xi B_1 S,$$

Here $\chi = M_{\perp}/B_1$ is the dynamic nuclear susceptibility; ξ is the filling factor of the coil by a sample, which takes into account that not the whole flow Φ_{add} crosses the transverse section of the coil. The appearance of Φ_{add} can be regarded as change of the inductance of the coil on the value of L_{add} :

$$L = \frac{\Phi + \Phi_{\text{add}}}{I} = \frac{B_1 S}{I} + \frac{4\pi \chi \xi B_1 S}{I} = L_0 + L_{\text{add}}.$$

Here I is the current in the coil; S is its cross section. Thus, in formula (2.4) instead of L one should write

$$L = L_0(1 + 4\pi \chi \xi),$$

and then instead of (2.4) one obtains

$$Y = \frac{\omega L_0 + i \cdot 4\pi \chi \xi R}{R\omega L_0}.$$

The voltage at the resonant circuit (U) is calculated as

$$U = \frac{I}{Y} = \frac{IR}{1 + i \cdot 4\pi \chi \xi Q},$$

where $Q = R/(\omega L)$ is the Q-factor of the circuit. In the absence of the signal of nuclear resonance $U = IR = U_0$. Since the value χ is of order 10^{-5} to 10^{-7} , then $4\pi \chi \xi Q \ll 1$, even if Q-factor $Q > 100$. Therefore we can put

$$U \simeq U_0(1 - i \cdot 4\pi \chi \xi Q). \quad (2.5)$$

Nuclear susceptibility is a complex value (see Sect. 1.5): $\chi = \chi' - i\chi''$, and we have

$$U = U_0[1 - 4\pi \xi Q(\chi'' - i\chi')] = U_0 + U_{\chi}, \quad (2.6)$$

$$U_{\chi} = U_{\chi''} - iU_{\chi'} = -4\pi \xi Q U_0(\chi'' + i\chi'). \quad (2.7)$$

It is seen from (2.4), (2.5), that the voltage on the resonant circuit is changed on the value of $U_{\chi''} = -4\pi \xi Q U_0 \chi''$, which is the *measure of the nuclear resonance absorption*.

The vector diagram illustrating the relationship component of $\vec{U}_0$, $\vec{U}_{\chi}$, $\vec{U}_{\chi'}$ and $\vec{U}_{\chi''}$ is shown in Fig. 2.8. Under the periodically coming nuclear resonance, the voltage on the resonant circuit changes by the value $U_{\chi''}$, causing its amplitude modulation, and the component $\vec{U}_{\chi'}$ determines phase change $\vec{U}_0$ at the angle ϕ . The modulation depth is small (about 10^{-2} to 10^{-4}), therefore, pre-amplification of the signal quickly leads to overload an amplifier, that is one of the main drawbacks of this spin detector. However, the simplicity of the scheme, the observation of the only absorption signal, the absence of complicated settings and relatively broad resonance curve of the

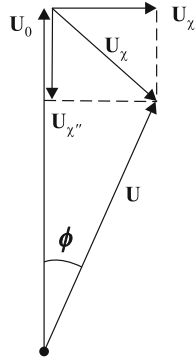


Fig. 2.8 The vector diagram of NMR signal components

resonant circuit, reducing the influence on the detector microphonics and temperature fluctuations, are advantages of this simple spin detector. To increase the modulation depth of U_0 by the NMR signal different versions of bridge circuits, one of which shown in Fig. 2.9 can be used. It should be kept in mind that the total compensation the voltage U_0 at the output of the bridge leads to the fact that the resulting signal is a mixture of dispersion and absorption signals: $|U_{\chi}| = (U_{\chi'}^2 + U_{\chi''}^2)^{\frac{1}{2}}$, that is inconvenient for the analysis of the spectra. Therefore, using the elements of C'_1 and C_2 a certain imbalance of the bridge can be achieved, so that the output voltage is $U = U_z + U_{\chi}$ (U_z is the voltage unbalance, $U_z \ll U_0$). If $|U_z| \gg |U_{\chi}|$, then $|U| = |U_z| + |U_{\chi}|$ is approximately equal to the projection of U on the direction of the vector U_z . Then we have

$$U \simeq U_z - U_{\chi''} \cos \phi - U_{\chi'} \sin \phi.$$

There are two extreme cases:

- (a) $\phi = 0, \pi$; $U = U_z \pm U_{\chi''}$;
- (b) $\phi = \pi/2, 3\pi/2$; $U = U_z \pm U_{\chi'}$.

Thus, depending on the type of the phase-balancing bridge, the amplitude modulation of the output voltage signal is caused by absorption or dispersion signals. The converse is obvious: if we measure some way phase shift of the voltage, than in the case (a) we obtain the dispersion signal, and in the case (b) the absorption signal is registered.

One of the original species of the bridge spin detector is a system of crossed coils (Fig. 2.10), which were used by F. Bloch. The axes of the transmitter (L_x) and receiving (L_y) coils are located at the angle 90° , so that, ideally, at such arrangement there is not a direct signal of RF generator from the transmitter coil in the receiving one. The field $\vec{B}_1$, which is produced by the coil L_x connected to the generator, excites

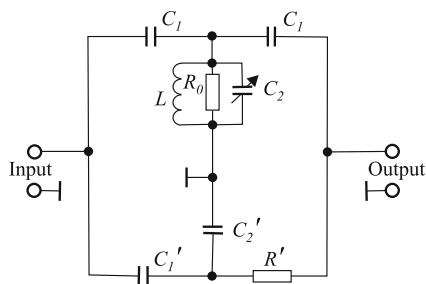


Fig. 2.9 The scheme of the RF-bridge circuits

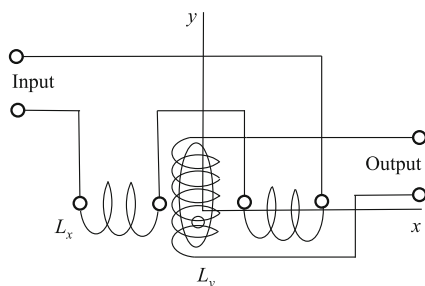


Fig. 2.10 The system of crossed coils by Bloch

in the sample the transverse component of the nuclear magnetization $M_{\perp} = M_x + iM_y$. A rotating component $M_{\perp}$ creates in the receiving coil L_y (with a cross section S and the number of turns of N) the alternating magnetic induction $\vec{B}_y = 4\pi \vec{M}_{\perp}$, which induces an emf at its ends:

$$U_y \simeq -4\pi NS(dM_y/dt) = \pm 4\pi NS(u \cos \omega t - v \sin \omega t). \quad (2.8)$$

Plus or minus signs depend on the sign of the gyromagnetic ratio of nuclei (see Sect. 1.5). It is seen from (2.8), that the induced emf in the coil consists of two component: $U_y(u)$ and $U_y(v)$. Thus, similar to bridge spin detectors, with the full compensation of the generator voltage at the output of the system with crossed coils there is a mixture of absorption and dispersion signals. To receive unambiguous signals of $U_{\chi'}$ or $U_{\chi''}$ it is necessary to submit a voltage from the generator to the coil L_y , that is realized by the amplitude or phase unbalance the system.

Let us consider spin detector of another type—weak oscillation generator (*autodyne*). For the first time it was used by E. K. Zavoiskii for the observation of electron paramagnetic resonance (in 1944), and in the following to record signals caused by nuclear magnetism. As it has been established, the appearance of the NMR signal changes the impedance and resonance frequency of parallel tuned LC -circuit. As a result the change of amplitude and frequency of the generated voltage is involved, that after appropriate detection can give signals absorption. One of the simplest schemes

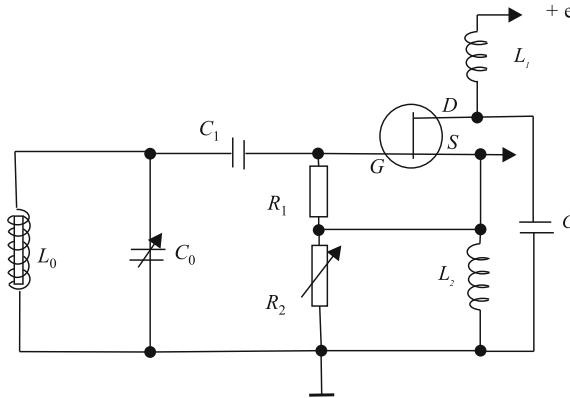


Fig. 2.11 The electrical schematic diagram of the autodyne

of this generator is shown in Fig. 2.11, where L_0 , C_0 are the inductance and capacity the resonant circuit; R_1 , R_2 are the resistances of feedback connection; L_1 , L_2 is the inductors; C is the capacitor of lower frequencies filter.

As such, the weak oscillation generator—*autodyne*—is a conventional RF generator of Hartley type, which theory is well-developed. An autodyne feature is that it generates a voltage with a small amplitude (tens or hundreds millivolts), and in this mode even very small changes of the parameters of the resonant circuit of the generator result in significant changes in the amplitude of the voltage generated by it. From the theory of the Hartley generator it is known that stable free oscillations occur when the values of feedback coefficient(k) exceeds a certain value (k_{cr}), i.e. at

$$k > k_{cr} = \frac{R_0 C}{SL} = \frac{1}{SZ_k}, \quad (2.9)$$

here R_0 and C are the parameters of parallel resonant circuit; Z_k is its equivalent resistance; S is the slope of characteristics of amplifier element (transistor). The dependence of the RF voltage U in the circuit from the coefficient feedback at the soft mode of generation is shown in Fig. 2.12. We have already noted that equivalent resistance of the parallel circuit decreases at nuclear magnetic resonance. According to (2.9), this leads to the increase of critical values of the feedback on Δk_{cr} . The entire plot of dependence of the voltage in the circuit on the feedback coefficient is shifted to the right (dashed curve), and for the established value of feedback coefficient k_0 the amplitude of the generator reduces on the value ΔU . The figure also shows that the change ΔU under the influence of the nuclear magnetic resonance will be the greater, the closer the feedback factor of the autodyne k_0 to k_{cr} . Consequently, the maximum sensitivity is achieved at the threshold of oscillations failure.

Due to their simplicity and relatively high sensitivity autodyne spin detectors were widely used by researchers in the early years of RF spectroscopy.

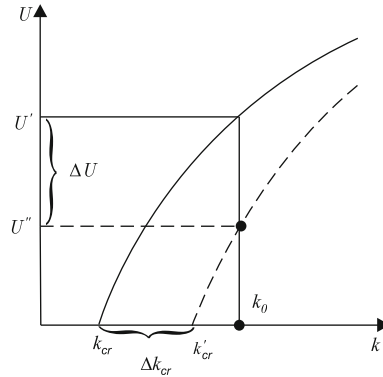


Fig. 2.12 The plot of voltage dependence of an autodyne on the values of feedback coefficients

2.3.2 Passage Through Resonance

In order to observe the spectral line of NMR it is necessary to organize the passage through resonance. This situation can be realized both with the periodic modulation of the static field B_0 near the resonant value $B_0 = \omega_0/\gamma$, and with the help of the modulation of the generator frequency. The latter method is less convenient, because it requires a large hardware efforts and has a number of shortcomings (for example, parasitic amplitude modulation is comparable to the magnitude of the signal). Recall that for the correct reproduction of the spectral shape of a line (see Sect. 1.6) it is necessary to fulfil two conditions: first, the RF amplitude of B_1 should be small enough to avoid saturation effects, and secondly, the rate of passage through the resonance should also be small, to avoid the distortion caused transient processes in the system of nuclear moments. As any physical system, the nuclear magnetization has some inertia, which can be described time constants T_1 and T_2 . The previous expressions for the components of the magnetization u and v describe a stationary state of the system, i.e. processes of formation $M_\perp$ and M_z are balanced by relaxation processes (the value of the field B_1 is small enough). If at any time to stop the passage through resonance, the values component u and v from that moment can be saved as long as one wishes. In other words, transverse component of the nuclear magnetization ($M_\perp$) “should follow” the direction of the field vector $\vec{B}_1$.

In the case of fast passage through the resonance, the “detachment” $\vec{M}_\perp$ from the vector $\vec{B}_1$ occurs and then $\vec{M}_\perp$ continues to precess independently with the variable angular frequency ω_0 . Since the frequency of the generator ω are the same, then in the spin detector there is the interference of two oscillations with frequencies ω and ω_0 . The result is beats with increasing frequency (“wiggles”). The phase difference between two signals in the case of a linear variation of the field $B_0(t) = B_0 + \frac{dB_0}{dt}t$ is

$$\phi(t) = \int_0^t \gamma[B_0(t) + B_0]dt = \frac{1}{2}\gamma \frac{dB_0}{dt}t^2 + \omega_0 t. \quad (2.10)$$

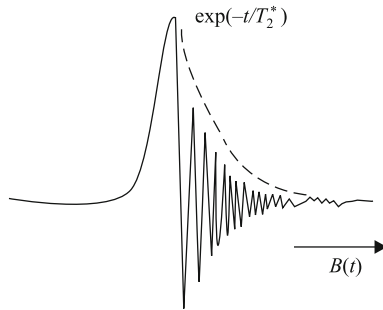


Fig. 2.13 The beats of NMR signal at the fast passage (wiggles)

The signal with beats is in the form, described by the expression (see also Fig. 2.13):

$$U = U_0 \exp\left(-\frac{t}{T_2^*}\right) \cos\left(\omega_0 t + \frac{1}{2}\gamma \frac{dB_0}{dt} t^2\right).$$

The exponential factor is introduced to take into account the decay the precession components $M_{\perp}$.

It was mentioned in Sect. 1.7.2 that the experimentally observed spectral line width of the magnetic resonance is characterized by the value T_2^* , which is determined by both the nature of the magnetic interactions in the matter, and inhomogeneity of the magnetic field B_0 . If the nature of field inhomogeneity B_0 is similar to the Lorentz distribution, the additional broadening of the signal can be described by a value $T_2'^*$, and the total width of the line—by the value T_2^* :

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'^*}. \quad (2.11)$$

It must be kept in mind that such a character of the broadening is not always valid and then (2.11) becomes incorrect. A detailed analysis of the solutions of the Bloch equations taking into account the passage speed of the line leads to the following criterion of the correct reproduction of the line shape:

$$\frac{dB_0}{dt} \leq \frac{1}{4\gamma T_2^{*2}}. \quad (2.12)$$

If NMR signals are observed in solids, characterized by very small T_2 , the criterion (2.12) is not determinative, but in this case the large width of the spectral lines $\Delta B \sim (1/T_2)$ allows one to use another approach for the choice of the amplitude of the sinusoidal modulation of the field B_m . As it can be seen from Fig. 2.14, if $B_m \ll \Delta B$, the signal at the output of the spin detector (in that situation is most often used an autodyne) is proportional to the slope of the line at the given point.

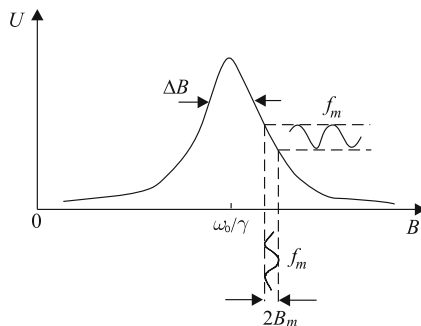


Fig. 2.14 The principle of the differential NMR passage

At the slow passage through the whole line (for example, due to changes in ω_0), the NMR signal U is proportional to the derivative of the line shape (*differential passage*). The exact correspondence to the first derivative is possible only if $B_m \rightarrow 0$, but in this case the amplitude $U \rightarrow 0$, so in practice, a distortion of the spectral line is allowed, which in principle can be taken into account with known modulation parameters. An additional advantage of the differential passage is the possibility of increasing the sensitivity of the device via a strong narrowing of a bandwidth of a receiving path, because the detected signal at the output receiver is close to sinusoidal modulation frequency f_m ($f_m \simeq 20\text{--}100$ Hz). Receiver, recorder and modulator are not different from appropriate series of radio equipment, so that blocks are not described here.

2.4 Pulse Methods of NMR Observation

2.4.1 The Action of the 90-degree Pulse

In Sect. 1.8 the result of RF pulse action on a system of nuclear moments is discussed in detail. For a visual representation of the majority of experimental methods based on pulse action, it is convenient to use the vector model of the interaction of the macroscopic nuclear magnetization $\vec{M}_0$ and field $\vec{B}_1$, created by the coil of a spin detector.

We introduce a rectangular coordinate system x, y, z , rotating around the axis of z , which is directed along the vector of the static field $\vec{B}_0$. We assume that frequency rotation ω is equal to the frequency of RF pulse. The result of the pulse action can be obtained from the Bloch equations. Let components of the field $\vec{B}_1$ in (1.56) during the time $0 \leq t \leq t_{\text{imp}}$ can be expressed as follows: $B_x = 2B_1 \sin \omega t$, $B_y = 0$, $B_z = B_0$. Then, neglecting relaxation processes during the pulse (pulse duration is chosen such that $t_{\text{imp}} \ll T_1, T_2^*$), one can write (1.56) in coordinate system rotating with the frequency ω :

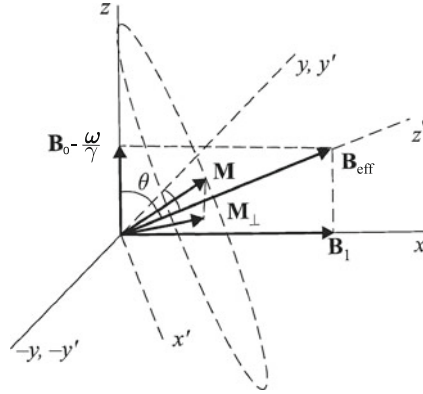


Fig. 2.15 The scheme of nutation of the magnetisation vector around the effective field B_{eff}

$$\begin{aligned} dM_x/dt &= \gamma(B_0 - \omega/\gamma)M_y, \\ dM_y/dt &= \gamma M_z B_1 - \gamma(B_0 - \omega/\gamma)M_x, \\ dM_z/dt &= -\gamma M_y B_1. \end{aligned} \quad (2.13)$$

The solution of (2.13) with the initial conditions $M_y(0) = 0$, $M_x(0) = 0$, $M_z(0) = M_0$ is:

$$\begin{aligned} M_x(t) &= M_{z0} \frac{\omega_1 \Delta \omega}{\omega_{\text{eff}}^2} (1 - \cos \omega_{\text{eff}} t), \\ M_y(t) &= M_{z0} \frac{\omega_1 \sin \omega_{\text{eff}} t}{\omega_{\text{eff}}}, \\ M_z(t) &= M_{z0} \left(\frac{\Delta \omega^2}{\omega_{\text{eff}}^2} + \frac{\omega_1^2 \cos \omega_{\text{eff}} t}{\omega_{\text{eff}}^2} \right), \end{aligned} \quad (2.14)$$

here $\omega_{\text{eff}}^2 = \omega_1^2 + \Delta \omega^2 = \gamma^2 B_1^2 + \gamma^2 (B_0 - \omega/\gamma)^2 = \gamma^2 B_{\text{eff}}^2$. Equations (2.14) describe the precession of the vector $\vec{M}$ around effective vector field $\vec{B}_{\text{eff}}$ —the so-called *nutation*. It is easily seen if we go to a system of coordinates $x'y'z'$, rotated relatively to the initial system on such an angle in the plane $(z0x)$, that the axis $0z'$ coincides with the direction of the vector field $\vec{B}_{\text{eff}}$ (Fig. 2.15). In the new system the components of $\vec{M}$ will be written as:

$$M_{y'}(t) = M_0 \frac{\omega_1 \sin \omega_{\text{eff}} t}{\omega_{\text{eff}}}, \quad M_{x'}(t) = M_0 \frac{\omega_1 \cos \omega_{\text{eff}} t}{\omega_{\text{eff}}}, \quad M_{z'}(t) = M_0 \frac{\Delta \omega}{\omega_{\text{eff}}}.$$

The vector $\vec{M}$ moves along the cone with angle θ determined by the deviation of frequency precession from the frequency of the RF pulse: $\cos \theta = \Delta\omega/\omega_{\text{eff}}$. For the small deviation ($B_1 \gg B_0 - \omega/\gamma$) $\omega_{\text{eff}} \simeq \omega_1$, i.e. the cone degenerates into a plane ($z0y$). If in addition the pulse duration

$$t_{\text{imp}} = \frac{\pi}{2\omega_1},$$

then at the time t_{imp} vector $\vec{M}$ will be in the plane ($x0y$) (90-degree pulse). It is evident that nuclear magnetization vector can be rotated to the plane ($x0y$) for sufficiently large detuning $\Delta\omega$. This requires only the condition $\Delta\omega \leq \omega_1$, i.e. the angle of the cone $\theta \geq 45^\circ$. The duration of the pulse, rotating the vector $\vec{M}$ into plane ($x0y$), can be found from the condition $M_z(t_{\text{imp}}) = 0$:

$$t_{\text{imp}} = \frac{1}{\omega_{\text{eff}}} \arccos \frac{\Delta\omega^2}{\omega_1^2}.$$

2.4.2 The Amplitude of Signal of the Free Induction

After the end of the 90-degree pulse we have the nonstationary state for nuclear magnetization (the vector $\vec{M}$ is perpendicular to vector field B_0 , the component $M_z = 0$). As it follows from Bloch equations (1.56), the behavior of the transverse components is described by functions

$$M_x(t) = M_0 \cos(\gamma B_0 t) \exp(-t/T_2^*),$$

$$M_y(t) = M_0 \sin(\gamma B_0 t) \exp(-t/T_2^*).$$

This behavior can be interpreted as a *free* (in the absence of the field $\vec{B}_1$) *precession* of the transverse component of the nuclear magnetization $M_\perp$ around the vector field $\vec{B}_0$.

Alternating magnetic flux in the coil of spin detector due to the precessing magnetization, in accordance with classical laws of electromagnetic induction, gives the emf of nuclear induction at the ends of the coil. For the correct estimation of the magnitude of this emf we use the well-known theory of electromagnetism: the reciprocity theorem for two circuits with a current. Represent an arbitrary element of a sample volume dV with nuclear magnetization $\vec{M}_0 dV$ in the form of an elementary contour ΔS with the current I : $\vec{M}_0 dV \equiv I \Delta S$. Another contour with the current I_1 is the coil of a spin detector. If we denote the flow of induction, created in the coil by the element $I \Delta S$ as Φ_m and the flow generated by the coil with the current I_1 through the element ΔS as Φ_1 , then, by the reciprocity theorem, $n\Phi_m/I = \Phi_1/I_1 = M$, (where M is the coefficient of mutual inductance of two circuits; n is the number of turns in the coil).

Since $\Phi_1 = \vec{B}_1 \Delta S$, we can write for $\Phi_m = \vec{B}_1 \Delta SI / (nI_1) = \vec{B}_1 \cdot \vec{M}_0 dV / (nI_1)$. Then the flow, generated in the coil from the whole sample, is:

$$\Phi = \frac{1}{nI} \int_{V_0} \vec{B}_1 \cdot \vec{M}_0 dV,$$

and for the nuclear induction emf we have

$$E = -n \frac{d\Phi}{dt} = -\frac{1}{I_1} \frac{d}{dt} \int_{V_0} \vec{B}_1 \cdot \vec{M}_0 dV \quad (2.15)$$

(where integration is performed over the whole sample volume V_0). For further we note that the field $\vec{B}_1$, created by the coil of spin detector, depends on the coordinates of the element in the sample and has, generally speaking, three components: $\vec{B}_{1z}$, $\vec{B}_{1x}$, $\vec{B}_{1y}$. Nuclear induction signal is generated only by precessing component of $\vec{M}_\perp$, perpendicular to the vector field $\vec{B}_0$, therefore in scalar product (2.15) only a component of the field $\vec{B}_\perp = \vec{B}_x + \vec{B}_y$ should be considered, since $\vec{B}_{1z} \cdot \vec{M}_\perp = 0$. The value of $\vec{M}_\perp$ is also dependent on the coordinates, since the field $\vec{B}_1$ of the 90-degree pulse is usually created by the same coil. Therefore, $\vec{M}_\perp = \vec{M}_0 \sin(\gamma B_1 t_{90})$ (t_{90} is the duration of a 90-degree pulse.) As a result for the initial signal amplitude, taking into account that the $\vec{B}_\perp(t) = \vec{B}_{\perp\max} \cos \omega_0 t$, we can write:

$$E_0 = -\frac{\omega_0 \vec{M}_0}{I_1} \int_{V_0} \vec{B}_{\perp\max} \sin(\gamma B_{\perp\max} t_{90}) dV. \quad (2.16)$$

Equation (2.16) is suitable for numerical calculations for arbitrary configuration of a sample and a coil, but for rough estimations the simplified expression can be obtained.

Suppose that a sample is only in the middle of a coil, where the field $\vec{B}_1$ is sufficiently homogeneous and almost independent of coordinates, and parameters of the 90-degree pulse is chosen so that $\sin(\gamma B_{\perp\max} t_{90}) = 1$. Then in (2.16) $\vec{B}_{\perp\max}$ can be taken outside the integral, using for it the well-known approximate expression: $B_{\perp\max} = \mu_0 \frac{n}{l} I_1$ (l is the length of the coil; $\mu_0 = 4\pi \cdot 10^{-7}$ H/m is the magnetic permeability of the vacuum). Note also that the spin-detector coil is a component of an resonant circuit with a quality factor Q , which is tuned to the frequency resonance ω_0 . As a result, we obtain an approximate formula:

$$E_0 \simeq \omega_0 M_0 \mu_0 \frac{n}{l} Q V_0, \quad (2.17)$$

here V_0 is the sample volume. For a typical case $B_0 = 1$ T, $V_0 = 10^{-6}$ m³, $Q = 50$, $n = 10$, $l = 10^{-2}$ m and from (2.17) it follows for the protons of water that the value of $E_0 \simeq 50$ mV.

Radiotechnical registration of such a signal does not present large difficulties, however, in many cases the signal can be significantly less. Thereby the quantitative

assessment of the real ratio of voltages of a signal and thermal noises, always presented in the electronic equipment, is very important. The main source of the noise component is the thermal noise of a coil of spin detector. An amplifier makes worse the initial S/N ratio, that is usually taken into account by introducing the so-called *amplifier noise factor* (F). The rms noise voltage of the parallel resonance circuit is given by the well-known Nyquist formula:

$$E_N = \sqrt{4kT_k R_0 \cdot \Delta f},$$

where T_k is the temperature of the coil; R_0 is the resonance circuit resistance at the operating frequency; Δf is the bandwidth of the receiving channel. Then the ratio of the rms voltages of signal and noise can be written in the form:

$$\frac{E_0}{E_N} \simeq \frac{\mu_0 \omega_0 M_0 (n/l) Q V_0}{(8kT_k F R_0 \cdot \Delta f)^{1/2}}.$$

Let us use for the calculation of R_0 the simplified expression:

$$R_0 = \omega_0 L Q \simeq \omega_0 Q \cdot 4\pi n^2 \frac{S}{l},$$

where S is the coil cross-sectional area of the coil, and substitute instead of M_0 its explicit expression (see (1.32)):

$$M_0 = \frac{N \gamma \hbar^2 I(I+1) \omega_0}{3kT}, \quad (2.18)$$

where N is the number of nuclei per unit volume. We assume that the sample temperature (T) is equal to the temperature of the spin detectors coil (T_k), then the S/N ratio can be calculated by the formula

$$\frac{E_0}{E_N} \simeq \frac{N \gamma \hbar^2 I(I+1) \mu_0}{12(kTF)^{3/2} (2\pi \Delta f)^{1/2}} \frac{\omega_0^{3/2} Q^{1/2} V_0 n^{1/2}}{V_L^{1/2}} \quad (2.19)$$

Here $V_L = lS$ is the volume of a coil. Formula (2.19) describes the basic dependence of the S/N ratio related to the NMR frequency (ω_0), the content of the nuclei in a sample ($V_0 N$) and the quality factor of the spin detectors coil (Q). It should be kept in mind that with the increase of the resonance frequency the ratio E_0/E_N increases less than $\omega^{3/2}$, as this reduces necessarily the number of turns (n) in a coil.

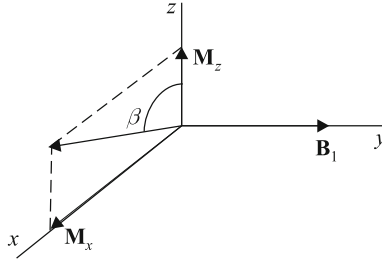


Fig. 2.16 The scheme of nutation of the magnetisation vector around $\vec{B}_1$ field

2.4.3 Principles of Fourier Transform in Nuclear Magnetic Resonance

It was noted in Sects. 1.7.1 and 1.8.2 that the Lorentzian shape of the absorption signal is the Fourier transform of the exponentially decaying signal of free induction (FID) after the of 90-degree pulse.

Consider once again the result of the exposure on the nuclear magnetization of a short pulse field $\vec{B}_1$, along the axis y of a frame rotating with the frequency of the external field ω . Let us assume, that the amplitude of the field $\vec{B}_1$ is large enough so by all possible detunings ($\Delta\omega = \omega_0 - \omega$) the rotation of vector $\vec{M}$ is almost in the plane (zx): $B_1 \gg \Delta\omega/\gamma$. If the angle of the nutation of the magnetization vector due to the pulse of duration t_{imp} (Fig. 2.16) is

$$\beta = \gamma B_1 t_{\text{imp}}, \quad (2.20)$$

then after the pulse we have:

$$\vec{M}_x(0) = \vec{M}_0 \sin \beta, \quad \vec{M}_y = 0, \quad \vec{M}_z(0) = \vec{M}_0 \cos \beta.$$

Further behavior of the components is described by obvious formulae:

$$\vec{M}_x(t) = \vec{M}_0 \sin \beta \cos \Delta\omega t \exp\left(-\frac{t}{T_2^*}\right),$$

$$\vec{M}_y(t) = \vec{M}_0 \sin \beta \sin \Delta\omega t \exp\left(-\frac{t}{T_2^*}\right)$$

or in the complex form:

$$\vec{M}_\perp(t) = \vec{M}_x(t) + i\vec{M}_y(t) = \vec{M}_0 \sin \beta \exp\left[i\Delta\omega t - \frac{t}{T_2^*}\right].$$

The free-induction signal $U(t)$, arising due to the precessing magnetization $\vec{M}_\perp(t)$, is also available in the complex form by using the principle of synchronous quadrature detection (see the following): $U = U_0 \sin \beta \exp[i \Delta \omega t - t/T_2^*]$. The Fourier transform of the signal

$$S(\omega) = \int_0^\infty U(t) \exp(-i\omega t) dt,$$

gives a complex spectrum:

$$S(\omega) = a(\omega) + ib(\omega),$$

where a and b are the already known (see Sect. 1.6) dispersion and absorption signals:

$$a = U_0 \sin \beta \frac{1/T_2^*}{(1/T_2^*)^2 + (\Delta\omega)^2}, \quad b = -U_0 \sin \beta \frac{\Delta\omega}{(1/T_2^*)^2 + (\Delta\omega)^2}.$$

It is clear that these signals are maximum if $\beta = \pi/2$ (90-degree pulse).

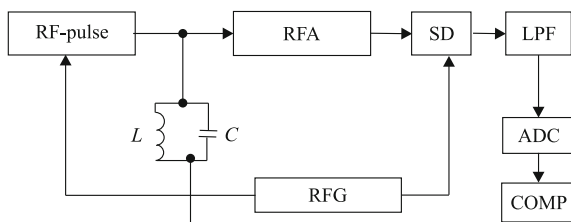
This correspondence has a deep physical meaning, since for any linear system, its frequency characteristic and the response to a single exciting pulse are connected by Fourier transform. Although both of these characteristics contain the same information, however, quite complex multiplet systems are serviceable and clear in the form of frequency characteristics of spectra. Note that the first publication about the obtaining of a NMR spectrum by Fourier transform of the free induction signal of nuclei was in 1958: A. A. Morozov, A. V. Melnikov, F. I. Skripov: "The method of free nuclear induction at low magnetic fields applied to some problems of spectroscopy with high resolving power", *Izv. AN USSR*, vol. 22, p. 1141–1144. In accordance to the level of computer technology the Fourier transform was performed with a mechanical arithmometer, so the calculation of a single spectrum was very time consuming. Therefore, the article of the authors of the Leningrad (now St. Petersburg) State University did not attract the attention of contemporaries, and the method was extended only with the appearance of the third generation of computers. The analysis shows that the method of the obtaining of spectra on the basis of Fourier transform of free-induction signals in the most cases gives significant advantages over the steady-state method of registration. Note the main ones:

1. Reducing the time of obtaining of the spectrum is greater, the greater the frequency domain spectrum compared with the width of a single line. Saving of time can be used for the accumulation of signals and, thus, for the improvement of S/N ratio.

2. Relatively rapid registration of a spectrum provides new possibilities for studying spectra of short-lived compounds or intermediate stages of chemical reactions.

3. Use of complex pulse sequences combined with Fourier-analysis allowed us to open new areas of research, such as two-dimensional NMR-spectroscopy, analysis of individual self-diffusion coefficients of spectral components using a pulsed gradient, MRI, etc.

Fig. 2.17 The block-scheme of the simplest pulse Fourier transform spectrometer



Let us consider some aspects of the experiment on registration of a spectrum based on pulsed excitation of a spin system.

Functional diagram of the simplest pulse Fourier transform spectrometer is shown in Fig. 2.17. RF pulses with controlled amplitude and duration periodically excite free-induction signals in the spin detector LC . After the preliminary amplification, the signal is mixed in synchronous detector (SD) with the reference signal of the frequency ω of RF generator. The signal from SD outputs with frequency $\omega_0 - \omega$ after pre-filtering (LPF) is digitized in the analog-to-digital converter (ADC) and recorded in the computer memory.

Pulse amplitude. It was shown in Sect. 2.4.1 that the motion of the magnetization vector $\vec{M}$ under the influence of field $\vec{B}_1$ in the case of frequency detuning ($\Delta\omega$), which is comparable to the value $\gamma \vec{B}_1$, occurs over the cone around the vector field $\vec{B}_{\text{eff}}$. The initial phase of component $M_{\perp}$ at the end of the pulse depends on the ratio of B_1 and $\Delta\omega/\gamma$. Thus, in the case of the NMR spectrum consisting of several lines with resonance frequencies ω_{0i} , generally speaking, it is impossible to provide the accurate turn of all vectors $\vec{M}_i$ at the same angle. Besides there will be different the initial phase of the precession of each component $M_{\perp}$. Synchronous—phase detection of signals of all components with following the Fourier transform will distort the shape of spectral lines, depending on their location in the spectrum, as well as the distortion of the correct ratio of intensities of components in a spectrum. These effects can be minimized if we fulfill the condition

$$B_1 \gg \frac{2\pi \cdot \Delta F}{\gamma}, \quad (2.21)$$

(ΔF is the full width of a spectrum). Thus the nutation of all vectors $\vec{M}_i$ will occur around the vector $\vec{B}_{\text{eff}} \simeq \vec{B}_1$ at the same angle. For example, the observation of the proton spectrum of ethanol with the width of about 750 Hz (at a frequency of 300 MHz) the field $\vec{B}_1$ must satisfy $B_1 \gg 1 \cdot 10^{-4}$ T, which is much less commonly used fields in experiments on measurements of T_1 and T_2 . But, for example, in the field of about 12 T the width of the ^{13}C spectrum can be ~ 30 kHz, and then $B_1 \gg 4 \cdot 10^{-3}$ T, which is not achieved in each spectrometer. The distortion of the spectral lines can be adjusted during the processing of the spectra in the computer.

The oscillator frequency can be set both outside of the limits of a spectrum (ΔF), and inside it. In the first case (Fig. 2.18a) all frequency differences $\omega_{0i} - \omega$ have one

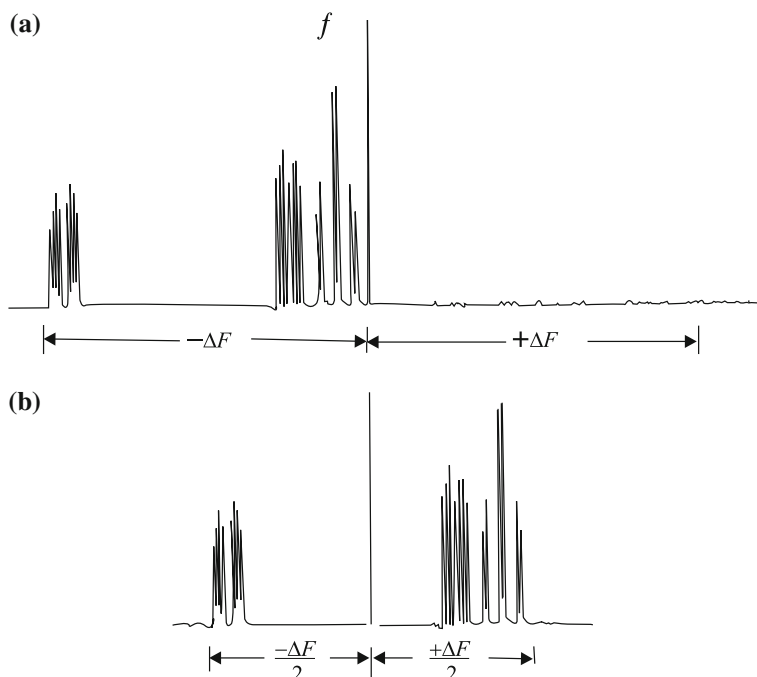
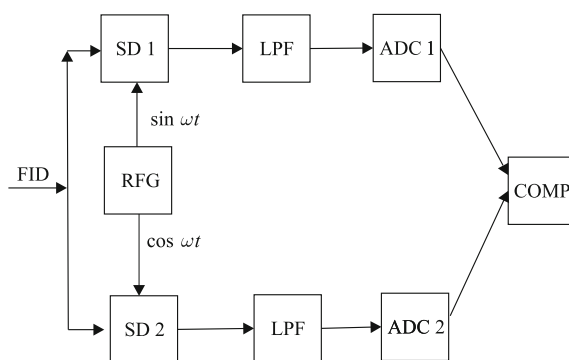


Fig. 2.18 The layout of the oscillator frequency to the frequency of a spectrum

Fig. 2.19 The block-scheme of a two-channel Fourier NMR spectrometer



sign, which allows to obtain a spectrum on a single-channel device, the block scheme of which was shown in Fig. 2.17. The disadvantage of a single-channel system is the decrease of the S/N ratio in $\sqrt{2}$ times, as after Fourier transform the noise is summed up in the band $\pm \Delta F$.

In modern instruments the two-channel schemes are generally used (see Fig. 2.19) with two reference voltages of the generator, shifted in phase by 90° . If we place

the frequency ω in the middle of the studied spectrum, then signals at the output of the synchronous detector will correspond to both positive and negative differences of $\omega_{0i} - \omega$ (see Fig. 2.18b), but the presence of two channels allows the correction of the places of all lines in a spectrum after complex Fourier transform. Additional advantage of the dual-channel scheme is the decrease of the required rate of the signal digitizing (see formula (2.22) below).

Coherent accumulation of pulse signals makes it necessary to maintain the values of ω at a fixed point of the spectrum (see Fig. 2.18), that can only be achieved by binding to the frequency ω_{0i} of certain line of NMR spectrum used as an internal or external reference. Without examining in details here the principles of nuclear resonance stabilization, we note only the obvious for these purposes: we could use the signal of dispersion, or a derivative of the absorption NMR signal. As an external standard one uses a separate ampoule with a substance which resonance line is located outside of an investigated spectrum. It is also possible to use an internal standard: the enough strong line of the spectrum or the test line of the specially selected inert substance which is added into an ampoule with the investigated solution. It is convenient to use deuterated solvents, because the resonance of deuterium can be a reference signal for field stabilization system.

Duration of the pulse. The product of the pulse duration and its amplitude defines the angle of rotation of the magnetization (β) in accordance with (2.20). The maximum signal is provided at $\beta = \pi/2$, but it is valid only for a single (rarely repeated) pulse. In cases, when it is necessary to average the signals for a certain number of repetitions during optimal time of the experiment, it must be considered the value of relaxation time T_1 . Suppose that $T_2^* \ll T_1$. If the period of repetition (T_0) is comparable to the value of T_1 , after a certain time the dynamic balance is established in a system. For the component $M_z(0_+)$ after the pulse, rotating it at the angle β , the following relation holds:

$$M_z(0_+) = M_z(0_-) \cos \beta,$$

where $M_z(0_-)$ is the component value before the pulse. For the components $M_z(T_0)$ at the end of the time T_0 one can write:

$$M_z(T_0) = M_z(0_+) + [M_0 - M_z(0_+)] [1 - \exp(-T_0/T_1)].$$

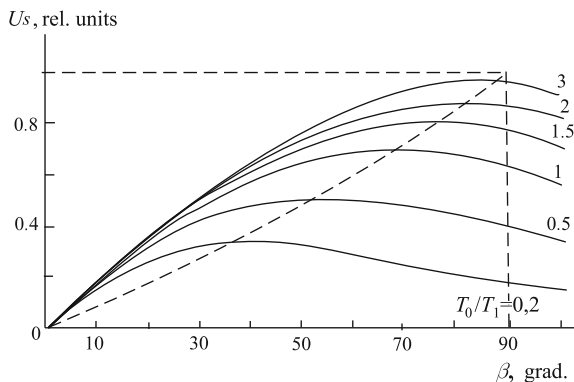
Since at the dynamic equilibrium $M_z(T_0) = M_z(0_-)$, then we have

$$M_z(0_-) = M_0 \frac{1 - \exp(-T_0/T_1)}{1 - \cos \beta \exp(-T_0/T_1)}.$$

The initial amplitude of the signal after the pulse depends on the magnitude of the transverse component:

$$M_x(0_+) = M_0 \frac{1 - \exp(-T_0/T_1)}{1 - \cos \beta \exp(-T_0/T_1)} \sin \beta.$$

Fig. 2.20 The dependences of the NMR signal on the rotation angle of magnetisation (β) at different relations T_0/T_1



The last formula implies that the signal amplitude is maximal at some β_{opt} :

$$\cos \beta_{\text{opt}} = \exp(-T_0/T_1).$$

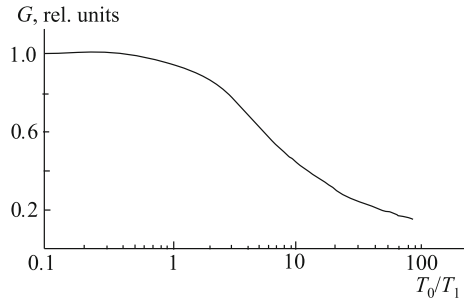
The dependencies of the relative amplitude of the signal (U_s) on the rotation angle (β) at different relations T_0/T_1 are shown in Fig. 2.20. The value β_{opt} is close to 90° only at $T_0/T_1 \geq 3$.

Signal to noise ratio. The possible improvement of the sensitivity of the method is determined by broadband pulse excitation of the spin system. In the stationary NMR spectroscopy for the spectra recording the successive passage through the resonance of each spectral lines is used. In this case, at any time the generator frequency corresponds to one point of the spectrum. A volume of information of a stationary method, in principle, can be improved if multiple generators and receivers tuned to different frequencies of a spectrum would be used, i.e. if we use a multi-channel spectrometer, but such a device in real situation is cumbersome and inconvenient. The excitation of a spin system with short pulse having a fairly wide spectrum is also equivalent to a multichannel spectrometer. If we exclude the time needed for Fourier transformation, it can be expected that the gain in the time, which is possible to obtain the spectrum, will depend on the ratio of the width of the whole spectrum to the width of a single line. The saved time may be used for coherent accumulation of signals. It is well known that at coherent accumulation the signal intensity is proportional to the number of repetitions (n), while the noise component increases proportionally $\sqrt{n}$. Let us consider the ratio of the signal amplitude to the rms amplitude of noises as a measure of sensitivity of the method. R. Ernst and G. Anderson showed that in the case of matched filters the ratio of the sensitivity of pulsed and stationary methods for the same measurement time is given by:

$$\frac{(S/N)_{\text{pulse}}}{(S/N)_{\text{stat}}} = 0.8 \sqrt{\frac{\Delta F}{\Delta}} G(T_0/T_1),$$

where ΔF is the width of a spectrum; Δ is the width of a single line, $\Delta = 1/(\pi T_2^*)$; T_0 is the pulse repetition period.

Fig. 2.21 The dependence of parameter G on T_0/T_1 (see text). Reproduced with permission from Rev. Sci. Instr., 37, 93 (1966). Copyright 1966, American Institute of Physics



The dependence of the function G on T_0/T_1 is shown in Fig. 2.21. It is evident that to increase the sensitivity the value of T_0 should be reduced. However, as we shall see below, the resolution of spectra in the method will be reduced. Therefore, the choice of the optimal duration of the pulse repetition depends on specific objectives: what is more important, to maximize the sensitivity or resolution ability in an experiment.

Sampling of NMR signal. To enter data on the NMR signal in the computer for the subsequent processing, the conversion of a continuous (analog) signal into digital form is required. This is done by the analog-to-digital converter (ADC). This procedure is a conversion of a continuous function $U(t)$, which describes the original signal, in a sequence of numbers (samplings) $\{U(t_n)\}$, $n = 0, 1, 2, \dots$, characterizing the amplitude of the signal in some equally spaced points in time. From the information theory it is known that for the correct registration of a sinusoidal signal in the digital form, its values should be obtained at least twice per a period. This means that for a signal of complex spectrum with the maximum frequency $F_{\max}$, the interval between samplings (Δt) must be

$$\Delta t \leq 1/(2F_{\max}).$$

The obtained value of sampling at the ADC output is usually presented as a binary code with a finite number of digits (N). The value of N depends on the design of the ADC and determines its resolution and dynamic range. Minimal value of the analog signal ($U_{\min}$), that can be displayed in digital form (quantization step) is $U_{\max}/2^N$, where $U_{\max}$ is the maximum allowed for the given ADC voltage. So, if $U_{\max} = 1$ V, $N = 12$, then $U_{\min} \simeq 120 \mu\text{V}$. Accordingly, the dynamic range of the ADC, defined as $D = U_{\max}/U_{\min}$, is the important characteristic of a system, because it determines the ability to register the signals of low intensity in the presence of a signal of high intensity. From this viewpoint it is desirable to apply ADC with maximal number of bits. Increasing this number usually leads to reduction of ADC speed, which is commonly characterized by the time conversion (t_{con}), during which occurs the setting of binary code corresponding to the input voltage. The value t_{con} must satisfy the condition:

$$t_{\text{con}} < \Delta t \leq 1/(2F_{\max}), \quad (2.22)$$

i.e. the dynamic range of the ADC (D) and the conversion time (t_{con}) must be matched with the expected width of a investigated spectrum. Note also that for two-channel device (see Fig. 2.19) $F_{\text{max}} = \Delta F/2$ in Eq. (2.22), so ADC speed can be reduced by factor of two with appropriate increasing the number of digits.

Optimization of parameters of spectral analysis. Possibility of separating the two close lines in the spectral range depends on the duration of the observation of the signal in the time domain. Thus, two neighboring lines with a minimum frequency difference ($\Delta\nu_{\text{min}}$) give the period of beats (T_{max}) in a free-induction signal:

$$T_{\text{max}} = 1/\Delta\nu_{\text{min}}.$$

This period can be observed if, at least, $T_{\text{max}} \leq T$ (T is the time of observation of the signal), that is $\Delta\nu_{\text{min}} \geq 1/T$. The end of the signal observation time (cut-off time) depends on the T_2^* , and with very good signal-to-noise ratio can be as high as $(2 \div 3)T_2^*$. Although the maximum resolution of the method is achieved at $T \gg T_2^*$, it should be kept in mind that the recorded time-domain signal is damped in time. The more we try to collect information, the more “noisy” it becomes. Here, as in any area of physical experiment, a contradiction between the desired sensitivity and resolution of the device is manifested. In practice we always must restrict the observation of a signal in limits of the order of T_2^* , and this means that, in fact, the Fourier transform is performed for the product of the nontruncated signal ($U(t)$) and the rectangular weighting function ($\Pi(t)$), which has the form

$$\Pi(t) = 1, \text{ for } 0 \leq t \leq T; \quad \Pi(t) = 0, |t| > T.$$

Corresponding spectrum $S_n(f)$ is the convolution of the original (undistorted) spectrum $S_0(f)$ with the Fourier transform of the rectangular function $\Pi(t)$:

$$S_n(f) = A \frac{\sin \pi f T}{\pi f T}.$$

Functions of the form $\sin x/x$ correspond to characteristic oscillations on the wings of spectral lines, which can mask more weak neighboring spectral lines. Figure 2.22 demonstrates an example of the dependence of oscillations on the ratio of cutoff time T and T_2^* . The amplitude of the oscillations (A) can be significantly reduced by multiplying an original signal in the time domain by a certain weight function (“window”) rather smoothly decreasing to the time $t = T$. This process is called *apodization* (the term came from optical spectroscopy) and in NMR spectroscopy in addition to reducing the oscillation, it can, as will be seen below, significantly affect the sensitivity and resolution of the Fourier spectrum. Among the most widely used apodization functions are the following (Fig. 2.23):

- (1) cosine window (curve 1): $H(t) = \cos \pi t/(2T)$;
- (2) Hanning window (curve 3): $H(t) = 0,5 + 0,5 \cos \pi t/T$;
- (3) Hamming window (curve 2): $H(t) = 0,54 + 0,46 \cos \pi t/T$.

Fig. 2.22 The effect of FID truncation on the amplitude of the oscillation in the wings of spectral lines

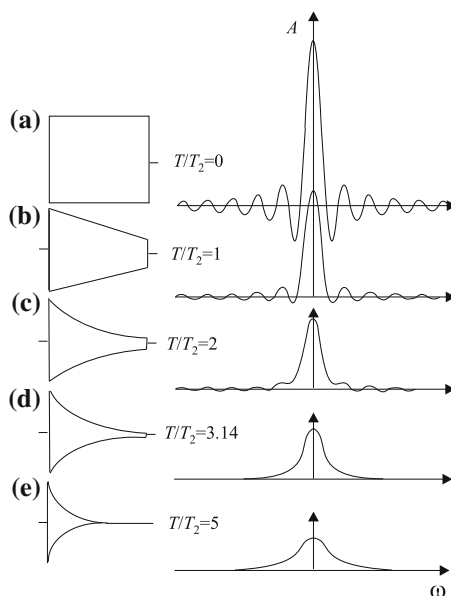
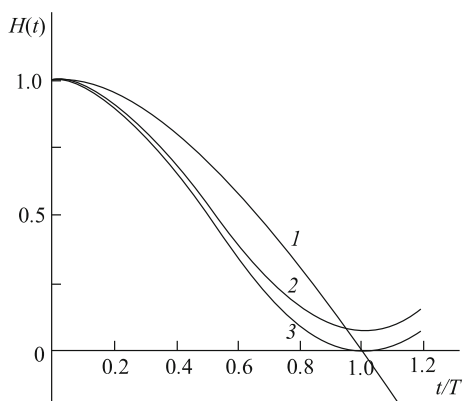


Fig. 2.23 The plot of apodization functions.

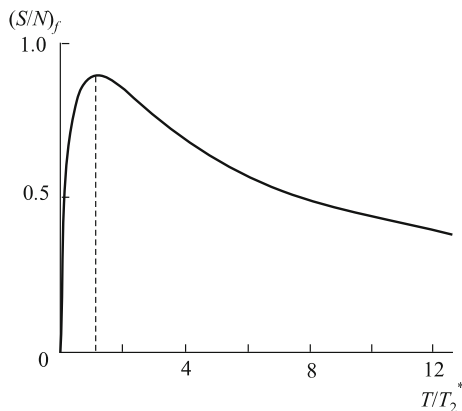
1—cosine window,
2—Hamming window,
3—Hanning window



Multiplication of the signal in the time domain on a decreasing apodization function leads to some broadening of spectral lines in the frequency domain (in 1.54–2 times), but also improves the ratio of signal-to-noise because the contribution of the noise voltage from the later parts of the signal progressively decreases. In this sense, the multiplication by an exponential-weighting function of form $\exp(-t/T_2^*)$ corresponds to the so-called *optimal* (or *matched*) *filter* in the time domain. Multiplication by $\exp(-t/T_2^*)$ keeps Lorentzian line shape, but broadens it twice.

Let us evaluate quantitatively the influence of the observation time (T) and the exponential filtering on the value of $(S/N)_f$ in the frequency domain for a single spectral line. The signal in the time domain is:

Fig. 2.24 The dependence of signal-to-noise value in the frequency domain for a single line on the ratio of the observation time (T) and relaxation time (T_2^*). Reproduced with permission from Prog. Nucl. Magn. Reson. Spec., v. 14, p. 27 (1980). Copyright 1980, Elsevier



$$U(t) = M_0 \exp(-t/T_2^*),$$

Then in the spectral domain

$$S(f) = M_0 \int_0^T \exp(-t/T_2^*) dt = M_0 T_2^* [1 - \exp(-T/T_2^*)].$$

Rms noise voltage can be written as

$$N(f) = \sqrt{\int_0^T [n(t)]^2 dt} = \bar{n} \sqrt{T},$$

where $n(t)$ is the current value of noise amplitude; $\bar{n}$ is the rms. For the ratio signal-to-noise in the frequency domain, we have:

$$\left(\frac{S}{N}\right)_f = \frac{M_0}{\bar{n}} \frac{T_2^*}{\sqrt{T}} \left[1 - \exp\left(-\frac{T}{T_2^*}\right)\right]. \quad (2.23)$$

It follows from (2.23) the clear link of the value $(S/N)_f$ and T_2^* : the more T_2^* , the narrower lines in the spectrum, and respectively greater the ratio $(S/N)_f$. At the same time, the dependence of $(S/N)_f$ on the ratio T/T_2^* has a maximum at $T/T_2^* \simeq 1.2$ (Fig. 2.24), that is also clear: if $T \gg T_2^*$, the signal information is virtually lost, but at the same time there is an accumulation of noise.

An apodizing function, in principle, can increase the resolution in spectrum if in the time domain this function prevents “decay” of a signal. In the simplest case, this function can be exponential with positive index of the form $\exp(bt/T_2^*)$. If $bt \simeq T_2^*$, then we obtain an undamped signal, that in the spectrum domain corresponds to the

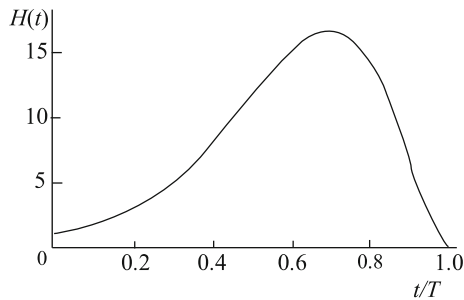


Fig. 2.25 The plot of Lorentz-Gauss apodization function

infinitely narrow δ -line. However, a line distortion and increasing noise make this procedure unreal. In literature there is a large number of functions that increase the resolution ability of the Fourier spectrum with an acceptable deterioration of the signal-to-noise ratio. The most optimum among them is Lorentz-Gauss transformation of the form $\exp(at/T - b(t/T)^2)$ (Fig. 2.25). At the initial stage of a signal a major role plays an increasing exhibitor, which improves the resolution, at the last stage the Gaussian character of a line with quickly damped wings is formed. Parameters a and b can be analytically optimized for a single line, but for a complex spectrum we must match them empirically.

Let us note one more possibility improving the character of the view of a spectrum. Because of the discrete Fourier transform the resulting spectrum is described by a set of equidistant points. The number of discrete points in the time domain is $N = T/\Delta t$, and with the $\Delta t = 1/(2F_{\max})$

$$N = 2F_{\max}T.$$

Fourier transform is a complex operation, i.e. $N/2$ points give real part of a spectrum and $N/2$ gives an imaginary one. Therefore the frequency interval between points in a spectrum is $\Delta = 2F_{\max}/N$. If the width of the observed lines is comparable with the Δ , then the spectrum may look like broken lines (Fig. 2.26). Of course, we can improve the view of a spectrum, if we increase the number N (preserving the value of $F_{\max}$, or Δt), but this is not always possible. Other possibility is the addition to data in the time domain of K zeros. This is equivalent to the prolongation of the signal observation, although this procedure does not give more information. If, for example, $K = N$, then the interval between points in the frequency domain will be halved. In principle, this addition can be infinitely big. In the limit we obtain quasicontinuous spectrum, but the restriction on this way mostly depends on the speed and memory of computers.

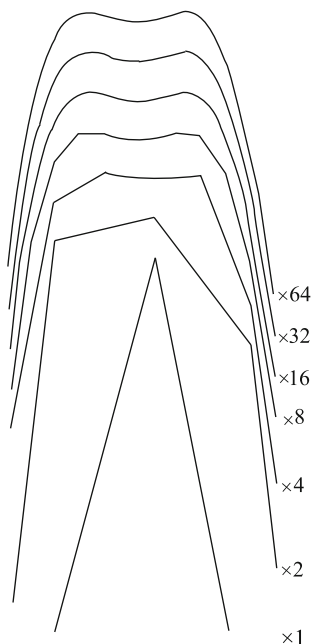


Fig. 2.26 The influence of the number of points in the time domain on the view of doublet spectrum

2.5 Measurement of Relaxation Times

The action of pulsed RF field on the system of magnetic moments is the most convenient way of removing the system from the equilibrium state. Monitoring the behavior of the system after pulses provides an analysis of the processes of establishing equilibrium, characterized by the relaxation time T_1 and T_2 . From the Bloch equations (1.56) it is easy to obtain expressions for component $M_z(t)$ and $M_\perp(t)$:

$$M_z(t) - M_0 = [M_z(0) - M_0]e^{-t/T_1}, \quad (2.24)$$

$$M_\perp(t) = M_\perp(0) e^{-t/T_2^*}. \quad (2.25)$$

Equations (2.24) and (2.25) give a general framework to formulate concrete ways to measure the times of longitudinal (spin–lattice– T_1) and transverse (spin–spin – T_2) relaxation. Let us remind that the evolution of the longitudinal and transverse components of the nuclear magnetization occurs independently and that the relaxation time T_2^* in the Bloch equation takes into account all kinds of the broadening of the spectral line of the nuclear magnetic resonance, including the influence of inhomogeneity of the static field ΔB_0 :

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \Delta B_0}{2}. \quad (2.26)$$

The consequences of this circumstance will be discussed in Sect. 2.5.2. As to the Eq. (2.24), then, taking the logarithm of it, we obtain:

$$\ln \frac{M_0 - M_z(t)}{M_0 - M_z(0)} = -\frac{t}{T_1}. \quad (2.27)$$

This expression reflects the fact that the rate of the relaxation process of the longitudinal component of the vector $\vec{M}$ is independent of the initial conditions. Pulse methods of the registration of nuclear magnetic resonance give the most universal way of measuring the relaxation times in a wide range of values: for T_2 —from units microseconds to hundreds of seconds, and for T_1 —from a few dozen microseconds to hundreds of minutes. Concluding the general comments, we note that all experimental effects in the study of nuclear magnetic resonance are associated with the registration of the circulating transverse component of the magnetization. So in order to get an information about the components of M_z , it is necessary to turn it into a component $M_\perp$ and the signal amplitude of nuclear magnetic resonance allow us to judge about the magnitude of components M_z .

2.5.1 The Measurement of the Spin–Lattice Relaxation Time

An initial non-equilibrium state at the nuclear magnetization can be created using the pulse, turning the magnetization at any angle. The restoration of the equilibrium longitudinal magnetization, according to (2.24), is described by one of the curves shown in Fig. 2.27. Curve 1 corresponds to the rotation of the magnetization vector at a small angle. It is most convenient to use the pulse rotating of the vector $\vec{M}$ on 90 or 180 degrees. In the first case (curve 2 in Fig. 2.27), the initial values of the components of magnetization is: $M_z(0) = 0$, $M_\perp(0) = M_0$. The precessing magnetization creates in the receiving coil a signal with an initial amplitude which is proportional to the value of the longitudinal magnetization at the moment preceding the pulse. If after the time τ we initiate the second 90-degree pulse, after it the signal occurs, an initial amplitude of which is proportional to the new value of the longitudinal components $M_z(\tau)$. From (2.24) with the initial conditions indicated, we obtain:

$$M_z(\tau) = M_0 \left(1 - e^{-\tau/T_1} \right),$$

and the expression (2.25) takes the form:

$$\ln \frac{M_0 - M_z(\tau)}{M_0} = -\frac{\tau}{T_1}. \quad (2.28)$$

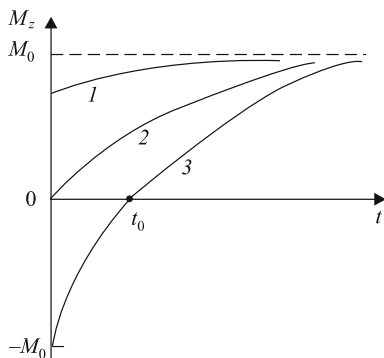


Fig. 2.27 The plot of restoration of the equilibrium of longitudinal magnetisation after pulse action: 1—The small angle of rotation. 2—The angle of rotation is 90° . 3—The angle of rotation is 180°

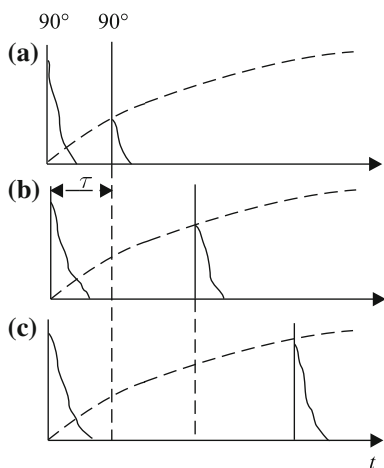


Fig. 2.28 The scheme of the E. L. Hahn experiment of T_1 measurement with pulse sequence $T - 90^\circ - \tau - 90^\circ - T - -$

Usually one builds function (2.28), recording the signals at different values of τ , and from the slope of the linear dependence determines T_1 . The scheme of the experiment is shown in Fig. 2.28. This method of measurements has been proposed by E.L.Hahn. If about the value of the M_z component corresponding to M_0 one judges by the amplitude of the free-induction signal after the first pulse, then between consequent series of $90^\circ - \tau - 90^\circ$ (see Fig. 2.28a) it is necessary to keep the interval $T \simeq 5T_1$ in order to the nuclear magnetization adopted the equilibrium value (at this condition, $M_z(T) = 0.993M_0$). Therefore, the total time of the experiment is rather large if $T_1 > 1$ s (to obtain the dependence (2.28) it is desirable to fix of about (20–30) M_z values for different values of τ). But at the stable operating hardware signal,

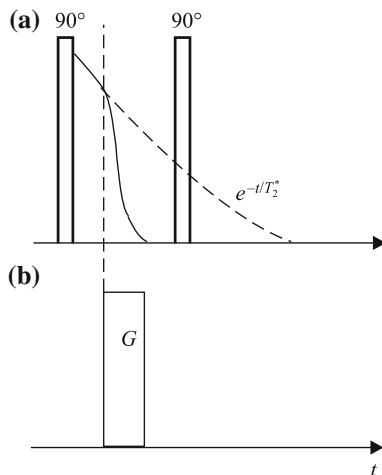


Fig. 2.29 A possible method to reduce the interval between the two pulses in the case of $T_1 \simeq T_2 \simeq T_2^*$. G is the pulse gradient

proportional to the equilibrium magnetization M_0 , can be determined in a separate experiment, and then interval between pairs of pulses can be significantly reduced, because after the first pulse the longitudinal magnetization disappears and its previous state does not matter. The applicability of the described method for measuring the time T_1 is limited by the case $T_1 \simeq T_2 \simeq T_2^*$, when the free-induction signal after first pulse prevents the signal registration after the second one at small intervals between pulses (it is impossible to set $\tau < T_2^*$). To neutralize this difficulty it is possible to create for a short time after the first 90-degree the pulse of magnetic field gradient B_0 with enough large value G (Fig. 2.29). The appearance of the gradient will result in a drastic reduction of the parameter T_2^* (see (2.24)). As a result, the second 90-degree pulse can be placed close to the first one (see Fig. 2.29).

If the first pulse rotates the vector of the nuclear magnetization at the angle 180° (i.e. it becomes against the vector field $\vec{B}_0$), then $M_z(0) = -M_0$ and $M_\perp(0) = 0$. Then the evolution of the components of $M_z(\tau)$ will correspond the curve 3 in Fig. 2.27. In this case, the relaxation function has doubled in magnitude, in comparison with the expression (2.28), that is significant for a small signal-to-noise ratio. From Fig. 2.27 it is clear that in this method of measurements (it is usually denoted as $180^\circ - \tau - 90^\circ$ or *inversion-recovery*) the longitudinal magnetization at some time t_0 is equal to zero. From (2.27) with $M_z(0) = -M_0$ we have $t_0 = T_1 \ln 2$, i.e. in this case it is possible to identify quickly T_1 without construction of the relaxation curve (*zero-method*). For a good signal-to-noise ratio (S/N) *zero-method* provides accuracy even higher than the sequence $90^\circ - \tau - 90^\circ$. For example, if $S/N > 100$ the error of T_1 measurements for protons of water is realized in the limits 1–2 %, the reproducibility of measurements—to 0.5 %. In addition, when working with amplitude detector in a receiver, the zero-method eliminates errors due to non-linearity of

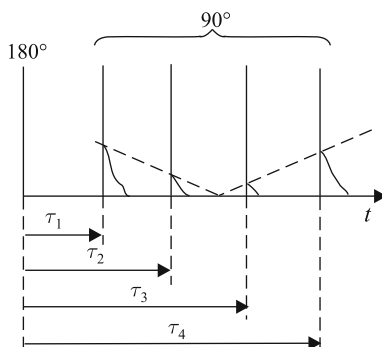
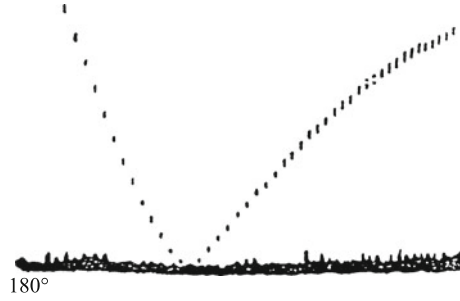


Fig. 2.30 The time diagram of NMR signals in T_1 measurements by pulse sequence $180^\circ - \tau - 90^\circ$

the detector at low signals. In Fig. 2.30 pulse diagram $180^\circ - \tau - 90^\circ$ with the peak amplitude detection of the signals is shown. For realization of the zero-method, it is necessary to have always $T > 5T_1$. Both described methods are associated with the considerable time consuming in the case of large relaxation times T_1 , since it is necessary to obtain a certain number of points on the relaxation curve, and it takes some time between pairs of pulses to bring the spin system in equilibrium state. To accelerate the process of measurements A. Csaki and G. Bene (1960) proposed after the first pulse to repeat periodically a group of three pulses: $90^\circ - \tau_0 - 180^\circ - \tau_0 - 90^\circ$. Within of this triple pulse sequence the nuclear magnetization is registered during the interval $2\tau_0$ and then it is returned to the initial state (relative to the beginning of the triple pulses), since the total rotation of the nuclear magnetization vector is 360° . In Sect. 2.5.2 the explanation will be given why this rotation should be composed with three stages: $90^\circ - 180^\circ - 90^\circ$. Here, we emphasize that the radio pulses used in this procedure must be coherent (i.e. with the same phase in the rotating frame). A necessary condition for the application of this sequence: $2\tau_0 \ll T_2$, otherwise irreversible decay of the magnetization due to the spin-spin relaxation leads to errors of measurements of T_1 . The oscillogram of signal series received for “one passage” using the triples pulses is shown in Fig. 2.31. In this oscillogram each point corresponds to the NMR signal from a triple pulses, which due to the receiver channel gating are not visible. Before the series of triple pulses in at time $t = 0$ the 180° -degree pulse is applied, that inverts the equilibrium nuclear magnetization (the signals are obtained with amplitude detection and therefore have a unipolar view).

There is quite a lot of modifications of pulse methods of measurements of the longitudinal relaxation time T_1 . The described methods can be considered as basic. Here we mention only two variants of the experiment in which one uses a continuous stream of RF pulses and which are appropriate in the case when $T_2 \ll T_1$. The first of these is known as the *progressive saturation*. In this version the continuous sequence of 90° -degree pulses separated by an interval τ is applied. After three–five pulses a stationary amplitude ($A(\tau)$) of free induction signals following after each pulse is

Fig. 2.31 An oscillogram of signal series using the triples pulses



established. If $\tau \gg T_1$, then $A(\tau) = A_0 \sim M_0$. For an arbitrary τ , we have:

$$A(\tau) = A_0 \left[1 - e^{-\tau/T_1} \right]. \quad (2.29)$$

The application of sequence progressive saturation can significantly save the time of the experiment, especially in those cases when it is required accumulation of weak signals. The method is simple to implement, as it only uses one kind of pulse, and in fact it is usual method of accumulation of signals in the Fourier transform nuclear magnetic resonance spectroscopy. Depending on the required accuracy of the experiment time T_1 can be calculated from (2.29) for some $\tau_1 \sim T_1$ with defined beforehand A_0 , or to plot the function (2.27).

Usually, all the methods measuring T_1 is based on the registration of amplitudes of nuclear magnetic resonance signals varying time intervals between pulses. However, there is an original method, in which one varies the angle of rotation of the nuclear magnetization vector by the RF pulse. Formally, this method is realized in the same way as well as method “progressive saturation”, but the registration of the amplitudes of nuclear magnetic resonance signals is performed at several angles of rotation of the nuclear magnetization vector. The M_z dependence on the rotation angle β is following (see also Sect. 2.4.3):

$$M_z(\beta) = M_0 \sin \beta \frac{1 - \exp(-\tau/T_1)}{1 - \cos \beta \exp(-\tau/T_1)}. \quad (2.30)$$

The function $M_z(\beta)$ in the form (2.30) is maximized when $\cos \beta = \exp(-\tau/T_1)$. From this equation it is easy to determine T_1 . In practice, the value of τ sets in the range $(0.3-0.8) T_1$ and a maximum amplitude of the signal is monitored at $\beta = 30-90^\circ$. The main advantage of this method is the quickness of the measurement performance, that determines perspectives of its application for systems which has a dependence T_1 on the time (for example, chemical reactions).

2.5.2 The Measurement of Spin–Spin Relaxation Time

The easiest way to measure the spin-spin relaxation time (T_2) is based on the registration of free induction decay signal after a single pulse, according to (2.25). Rotation of the vector of nuclear magnetization can be done at any angle (it changes only the initial value of the transverse component of the magnetization $M_{\perp}(0)$), but to obtain maximum signal-to-noise ratio is appropriate to apply the 90-degree pulse. Taking logarithm of (2.25), we obtain:

$$\ln \frac{M_{\perp}(t)}{M_0} = -\frac{t}{T_2^*}. \quad (2.31)$$

This method can be applied in the case when the magnetic field inhomogeneity ΔB_0 does not make a significant contribution to the line width (see (2.26)), i.e. when $T_2^* = T_2$. It is easy to estimate that, if the error of the measuring time T_2 is admissible within $N\%$, then the maximum value of T_2 in samples should not exceed a certain limit in accordance with the formula:

$$T_{2\max} < \frac{N}{50} \frac{R}{\omega_0}, \quad (2.32)$$

where R is the resolution magnetic system ($B_0/\Delta B_0$); $\omega_0 = 2\pi\nu_0$. Formula (2.32) is obtained under the supposition that $N \ll 100$, i.e. the inhomogeneity of the magnetic field makes a small contribution to the total width of a line of the nuclear magnetic resonance, because otherwise measurements are meaningless. To illustrate the importance of the problem, we estimate $T_{2\max}$ for spectrometer of the middle class: $R = 10^9$, $\nu_0 = 300$ MHz. If an error in the measurement of T_2 is admissible within 5%, then we obtain from (2.32) $T_{2\max} < 0.05$ s, that means the impossibility of measurements for a wide range of objects (for example, at room temperature for water protons $T_2 \simeq 3$ s).

It was found, however, that the dephasing of the precession of the nuclear magnetization of a sample because of the inhomogeneity of the magnetic field is reversible. E. Hahn showed that if to act on a sample with the two RF pulses at an interval of τ , which rotate the vector $\vec{M}$, respectively, on the angles β_1 and β_2 , then after the time τ after the second pulse the nuclear induction signal appears in the shape composed of two mirror signals of free induction decay (Fig. 2.32). This signal is called a *spin echo*. Analytical description of this phenomenon holds in Sect. 1.3. We now carry out more visual analysis based on the vector model, taking into account the relaxation processes.

We can in mind divide a sample on so small parts, within which the field B_0 can be considered as homogeneous, i.e. within each parts is fulfilled the condition $T_2 \ll 2/(\gamma \Delta B_{0i})$, where ΔB_{0i} is the field inhomogeneity i -th part of the sample. Let the nuclear magnetization of i -th part is characterized by the value of $\vec{m}_i$. Then $\vec{M} = \sum_i \vec{m}_i$. For each magnetization $\vec{m}_i$ the Bloch equations are valid, which now contains the true time of the spin-spin relaxation of nuclei. However, the frequencies

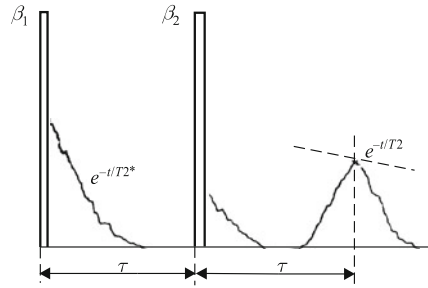


Fig. 2.32 The time diagram of NMR signals in the case of two pulse sequence (the angles of rotation approximately 90°)

of nuclear magnetic resonance $\omega_i(x, y, z)$ in each i -th part will be somewhat different from the average rate ω_0 . Then the value of $M(t)$ will parametrically depend on the angles of rotation of the magnetization vector under exposed pulses and on $\Delta\omega_{0i} = \omega_0 - \omega_i(x, y, z)$. After summing we can get that at the time of 2τ the signal of nuclear magnetic resonance arises again, the maximum amplitude of which is given by (actually after integrating over all $\omega_i(x, y, z)$):

$$A(2\tau) = A(0) e^{-2\tau/T_2}, \quad (2.33)$$

where $A(0)$ is the value which depends on the angles of rotation of the nuclear magnetization vector under the influence of the first and second pulses.

The relaxation decay does not depend on the angles rotation of the vector, but in practice one uses the sequence of pulses $90^\circ - \tau - 180^\circ$, after which arises an echo signal with the greatest amplitude. A diagram of the appearance of echo signals after two pulses: $90^\circ - \tau - 180^\circ$ is shown in Fig. 2.33. After the 90 -degree pulse the orientation of the vectors $\vec{m}_i$ is perpendicular to the vector of the external field $\vec{B}_0$ (see Fig. 2.33a), and these vectors will precess around the vector $\vec{B}_0(x, y, z)$, each with its own frequency $\omega_{0i} = \gamma B_0(x, y, z)$. The vectors $\vec{m}_i$, for which $\omega_i = \omega_0$, will be fixed in the rotating frame (position 2 in Fig. 2.33b), others will overtake the system coordinates (position 1), or lag behind (position 3). After some time the vectors $\vec{m}_i$ will unfold in a fan, which symbolized in Fig. 2.33b by three discrete positions. The total magnetization will decrease with time constant T_2^* , but the magnitude of each vector $\vec{m}_i$ decays with a time constant of T_2 . If at the time τ we apply a RF pulse in order to turn all the vectors around the vector field $\vec{B}_1$ at 180° , then their relative position is reversed (see Fig. 2.33c). The parameters of such a pulse satisfy:

$$\gamma B_1 t_i = \pi.$$

The vectors $\vec{m}_i$ will continue to precess at the same frequency, and through the time τ after the second pulse, they will be in-phase (see Fig. 2.33d). At this moment the signal induced in the receiver coil will be maximal (spin echo). After $t = 2\tau$ the

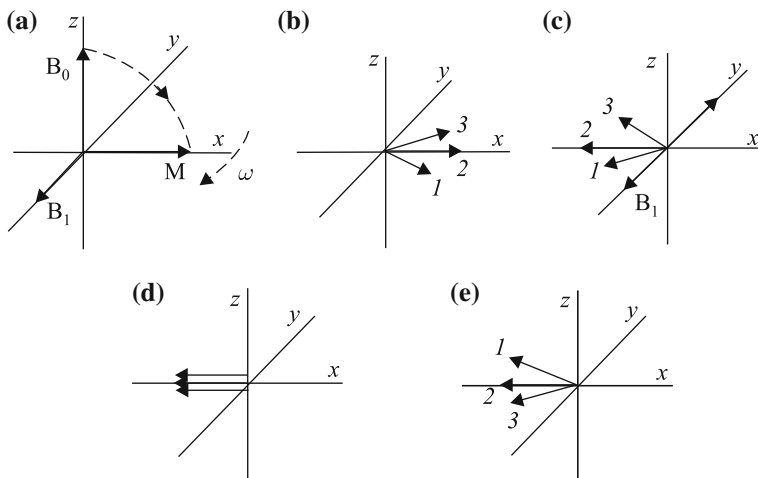


Fig. 2.33 The vector diagram of the appearance of echo signals after two pulses $90^\circ - \tau - 180^\circ$

echo signal decreases due continuing dephasing $\vec{m}_i$ (see Fig. 2.33e). Since during the time 2τ irreversible decrease of the value of vectors $\vec{m}_i$ because of the spin-spin relaxation takes place, the amplitude of the echo signals always less than the free induction signal after the first pulse and depends on time according to (2.33). Repeating the sequence of $90^\circ - \tau - 180^\circ$ with different τ , it is easy to obtain the dependence

$$\ln \frac{A(2\tau)}{A(0)} = -\frac{2\tau}{T_2}$$

and to compute T_2 from it. Naturally, that between pairs of pulses it is necessary to wait time $T = 5T_1$, in order to the spin system comes to equilibrium.

Scheme of the echo signal (see Fig. 2.33a–e) allows us to understand the need to split a 360-degree rotation of the vector magnetization into three steps ($90^\circ - 180^\circ - 90^\circ$) when measuring T_1 by method of A. Csaki and G. Bene. Indeed, the third (90-degree) pulse turns the phased magnetization (see Fig. 2.33d) along the vector field B_0 , i.e. the magnetization takes the orientation, which it had before the first 90-degree pulse.

This description of the process echo signal valid only in the case when the spatial coordinates of each element $\vec{m}_i$ do not depend on time, at least in the interval from the first pulse to the echo, that is for the absence in a sample of noticeable translational diffusion or macroscopic flows of the magnetic moments. Due to fast self-diffusion of molecules in low-viscosity liquids the precession phase shift of the vectors $\vec{m}_i(x, y, z)$ is different for time intervals between pulses and between the second pulse and the peak of an echo signal, i.e. frequency $\omega_i(x, y, z)$ are, to some degree, random functions of time. Analysis of the Bloch equations with taking into

account the diffusion of nuclear magnetization in the presence of linear changes of the field B_0 in a sample:

$$B_z = B_0 + zG_0$$

(G_0 is the magnetic field gradient in a sample) results the following dependence of the amplitude of the echo signal on the time:

$$A(2\tau) = A(0) e^{-2\tau/T_2} e^{-\frac{2}{3}D\gamma^2 G_0^2 \tau^3}. \quad (2.34)$$

where D is the diffusion coefficient. Analysis of the relation of exponents in (2.34) allows us to estimate the possible limit of values T_2 , which can be measured without any significant errors in the presence of fast molecular motion:

$$T_2 \ll 4 \left(\frac{R^2 d^2}{\omega_0^2 D} \right)^{\frac{1}{3}} \approx \left(\frac{16 d^2 T^{*2}}{D} \right)^{\frac{1}{3}}, \quad (2.35)$$

Here are $R = B_0/(G_0 d)$ is the resolving power of a magnet; d is the diameter of a sample. At the derivation of (2.33) it was assumed $\tau = T_2/4$. If $d = 1$ cm, $\nu_0 = 300$ MHz and $R = 10^9$, then for substances having a viscosity of water ($D = 2 \cdot 10^{-5}$ cm²/s), we get $T_2 \ll 100$ s, i.e. the condition significantly better than for a single-pulse technique (see (2.32)). However, the formula (2.35) makes quite strict limits of applicability double-pulse technique for measuring time T_2 using devices equipped by magnets with a mean resolving power (for example, even at $R = 10^7$ it is impossible to measure the relaxation time of water protons, for which $T_2 \simeq 3$ s). H. Carr and E. Purcell (1958) showed that the echo signal can be repeated many times, if instead of a single 180-degree pulse to form a package of n pulses at an interval of 2τ . In this case, at the intervals $(2n)\tau = t$ echo signals will occur, the amplitudes of which (A_n) decrease in accordance with the following law:

$$A_n(t) = A(0) e^{-t/T_2} e^{-D\gamma^2 G_0^2 \tau^2 t/3}. \quad (2.36)$$

By reducing repetition period of 180° pulses we can make the diffusion attenuation as small as wished.

The amplitude of the spin echo can change in the presence of convection currents in the fluid, which often occur because of the gradient temperature within a sample under high temperatures. In this case, macroscopic parts of a sample are moved through areas of the magnetic fields with different values of B_0 . If one uses a sequence of coherent pulses 90° – 180° – 180° – ... (sequence Carr-Purcell), the amplitudes of the odd echo signals are less than even, and a situation can be realized when every odd echo disappears altogether. This effect should be taken into account when measuring the coefficients diffusion, but it can be the subject of a separate study.

2.5.3 The Selective Measurement of the Relaxation Time T_1 and T_2

It was assumed in Sects. 2.5.1 and 2.5.2 that the nuclear magnetic resonance spectrum consists of a single line. The presence of nuclei electron shielding, spin–spin interactions or physicochemical heterogeneity in a substance results in the appearance of different lines in NMR spectra, which can be attributed to certain nuclear macroscopic magnetization $\vec{M}_k$, characterized by a relaxation time T_{1k} and T_{2k} (in the case of unresolved spectral lines the possible difference relaxation characteristics also needs to be considered). The most common approach to the task of determining the relaxation characteristics relating to individual spectral lines is associated with obtaining NMR spectra using the pulse technique in conjunction with the Fourier transform of free nuclear induction signals arising after pulse acting on the spin system. To do this, it is necessary to register the intensity of the spectral lines on the delay time between pulses, changing the orientation of the nuclear magnetization.

Measurements of T_{1k} for individual spectral lines are usually made using of the sequence $180^\circ - \tau - 90^\circ$, and the Fourier transform of the free induction signal after the second (90 degree) pulse, varying τ . Based on the dependence of the amplitude of each line of a spectrum from τ it is possible to evaluate T_{1k} .

When measuring the T_{2k} in complex spectra one uses Carr-Purcell sequence with the Fourier transform of the echo signals at different values of t .

Of course, the indicated here ways of measurements T_{1k} and T_{2k} can only be realized with the help of modern NMR-spectrometers with high-speed computers.

Another variant of measurements of relaxation characteristics of the individual components of a spectrum is to choose the pulse parameters in such a way as to affect only one line (or one group lines) in a spectrum. These pulses are called *selective*. The simplest way to implement them is to apply pulses, the spectrum (S_i) of which satisfies the expression:

$$\Delta\omega_l \ll S_l \ll \Delta\omega_{\sigma k}, \quad (2.37)$$

where $\Delta\omega_l$ is the width of an individual line in a spectrum; $\Delta\omega_{\sigma k}$ is the frequency difference between the investigated and the nearest (k) lines in a spectrum. The condition (2.37) cannot always be satisfied and then we have to use more complex pulse program or tolerate with experimental error.

As already indicated, the more difficult case is when NMR spectral lines are not resolved. In this case, the relaxation functions are complex. For example, Fig. 2.34 shows the relaxation function for the transverse component of the protons magnetization of water, saturating a porous medium. In this case, the relaxation function is well described by the sum of two exponential functions:

$$F(t) = \sum_{i=1}^2 F_i(0)e^{-t/T_{2i}}. \quad (2.38)$$

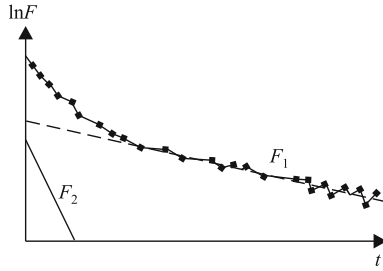


Fig. 2.34 An example of two components spin-spin relaxation (water in porous medium)

For more complex situations, the number of exponential components in (2.38) will be larger and their separation is problematic.

2.6 The Measurement of Coefficients Translational Diffusion

It follows from (2.34) that the amplitude of an echo signal in two-pulse sequence depends on both time T_2 and self-diffusion coefficient D , where the dependence on the pulse interval τ in the diffusion component significantly bigger: τ^3 . Therefore with the appropriate choice of the value τ the ratio of the relaxation and diffusion components in the decay of an echo signal can be varied. Let us estimate the admissible values of the coefficient D , which can be measured in conditions of a stationary gradient. If we assume that at the time $2\tau = T_2$ the influence of self-diffusion process on the attenuation of an echo signal must be at least of the same order as due to the relaxation. We can write:

$$\exp \frac{-2\tau}{T_2} \geq \exp \left(-\frac{2}{3} D \gamma^2 G_0^2 \tau^3 \right).$$

Hence, it follows the evaluation the minimum measurable coefficient of self diffusion:

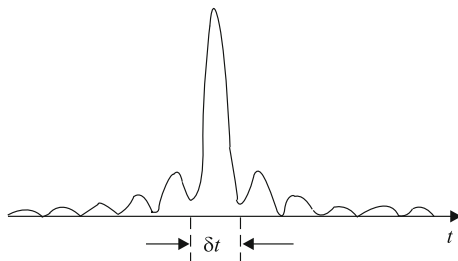
$$D \geq \frac{12}{T_2^3 \gamma^2 G_0^2}. \quad (2.39)$$

“Apparatus” relaxation time T_2^* can be approximately expressed in terms of field inhomogeneity $G_0 d$ in a sample of a diameter d as $T_2^* = 2/(\gamma G_0 d)$, so (2.39) can be rewritten in the form:

$$D \geq 3d^2 \frac{T_2^{*2}}{T_2^3}. \quad (2.40)$$

Minimum permissible value of T_2^* mainly depends on the capabilities of equipment used, because the decrease of T_2^* requires the corresponding increase of the

Fig. 2.35 The shape of a spin-echo signal for the cylindrical sample in the presence of the magnetic field gradient



bandwidth of receiving channel of a relaxometer. We should also bear in mind the inevitable worsening of signal/noise ratio. For a typical example, we can put $T_2^* = 10^{-4}$ c, $d = 10^{-2}$ m, then we obtain $D \geq 3 \cdot 10^{-12} \text{ m}^2 \text{ c}^{-1}$. As seen from (2.40), to extend the limits of measurable values of D it may be achieved by reducing the diameter of sample ampoules. The theoretical limit for the minimum value of an ampoule diameter can be estimated from the diffusion relations $\langle r^2 \rangle = 6D\tau$. To eliminate the effect of the walls (restricted diffusion), we must have:

$$d \gg \sqrt{6D\tau}.$$

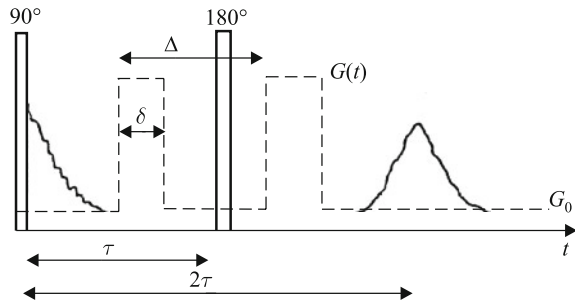
Let's do the numerical estimation for the water at 20°C ($D_{\text{H}_2\text{O}} = 2.03 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$). If the time between pulses is 10 ms, then the diameter of ampoules should be more than 10^{-4} m, which is always performed in the experiment. Therefore, the minimum diameter of ampoules is defined by the necessity of realization of the desired level of sensitivity or some other technical reasons.

In practice, the self-diffusion coefficient is measured on the basis of the Eq. (2.34), from dependence of the echo amplitude $A(2\tau, G_0)$ on the value magnetic field gradient G_0 for fixed τ . The gradient G_0 is typically realized with the help of current-carrying conductors located at the periphery of a sample. The value of G_0 , in principle, can be calculated knowing the geometry of the conductors or from the shape of an echo signal. In the presence of the magnetic field gradient in the echo envelope appear characteristic beats with a period that is associated with the size of the sample and the value G_0 (Fig. 2.35). Thus, if the sample is cylindrical, and the gradient vector G_0 is directed perpendicular to its axis, the interval between the two minima in the echo signal:

$$\delta t = \frac{15,3}{G_0 \gamma d} \quad (2.41)$$

(where d is the diameter of a sample.) Keep in mind that calculated values of the G_0 are insufficiently correct, since formula (2.41) holds for some idealized conditions (a sample is the infinitely long cylinder, a gradient coils do not create inhomogeneities of higher order (see Sect. 2.2). Corrections can be made, for example, from the measured value D of water at a fixed temperature ($D = 2.299 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at $t = 25^\circ\text{C}$).

Fig. 2.36 The time diagram of spin-echo signals at $90^\circ - \tau - 180^\circ$ RF pulse sequence with the pulse magnetic field gradient $G(t)$



The basic restriction of the method with a stationary gradient, considered in previous cases, is the inability of registering of NMR signals in the presence of large gradients due to the excessive shortening of the duration of these signals: $T_2^* = 2/(\gamma G_0 d)$. It should also be taken in to account a requirement, imposed on the amplitude of the RF field B_1 when applying the 90-degree pulse:

$$B_1 \geq G_0 d. \quad (2.42)$$

The violation of this condition leads to an additional decrease of the amplitude due to unequal angles of rotation of nuclear magnetization vectors which are inherent to the individual elements of a sample. These conditions lead to the fact that the real boundary of a minimum measurable quantity D is near $10^{-11} \text{ m}^2 \text{ s}^{-1}$, which is only of two orders of magnitude less than the self-diffusion coefficient for water.

Significant expansion of these boundaries can be achieved if, as it was first proposed by E. Stejskal and I. Tanner (1965), magnetic field gradients are created in the form of pulses, located in the intervals between the RF pulse and the echo signals. In this case, in the condition (2.42) instead of $G_0 d$ the natural inhomogeneity of the magnet should only be considered, which can be very small. In addition, the echo signal is also observed in a relatively uniform field, and therefore limitations on the bandwidth of a receiver become softer.

The scheme of the experiment is shown in Fig. 2.36, where besides a standard pulse sequence $90^\circ - \tau - 180^\circ$ the dotted line shows the dependence of the magnetic field gradient on the time. Analysis yields the following dependence of the echo amplitude $A(2\tau, G)$ on the parameters of the pulse sequence ($G_0 \ll G$):

$$A(2\tau, G) = A(0) \exp \left[-\gamma^2 G^2 D \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right],$$

Here $A(0)$ is the amplitude of the echo signal in the absence of the gradient; δ and Δ are, respectively, the gradient pulse duration and the interval between gradient pulses, with the condition $\Delta \gg \delta$. In typical cases the value of δ can vary from tens of microseconds to tens of milliseconds, the value of Δ —from a few milliseconds to a few seconds. The value of the gradient G_{max} , is mainly determined by the specific

features of the equipment and can be up to 50 T/m. The minimum measurable value of D can reach the order of $10^{-15} \text{ m}^2 \text{ s}^{-1}$.

To determine the self diffusion coefficient it has been registered the dependence $\ln A(2\tau, G)/A(0)$ on G^2 , δ^2 or Δ in accordance with the goals of experiment. For example, changing parametrically the interval Δ , we can study the diffusion in the presence of confinements when the mean diffusion path of particles is comparable with the size, limiting the scope (for example, a fluid in the porous environment or biological membrane).

Apart from the obvious advantages the method of pulsed gradient is rather difficult to implement for many reasons. We point out the basic ones. The analysis shows that for the correct reproduction of the signal amplitude the area of two gradient pulses must differ not more than 10^{-3} to $10^{-4} \%$, which is a rather complex radio engineering task. Furthermore, powerful pulses of current in the gradient coils cause the appearance of eddy currents in the magnet pole pieces and other metal parts and strongly distort the spatial and temporal gradient configuration that eventually also distort the measurement results. Solution of this problem may lie in the design of more complex configuration of gradient coils without a field outside a sample, as well as in the formation of more complex pulse sequences.

2.7 Spin Echo in a Three-Pulse Sequence

There is quite a simple pulse sequence, consisting of three 90-degree pulses, the consideration of which is appropriate in a separate section due to historical and methodological points of view. This sequence was described in the first paper of E. Hahn devoted to the phenomenon of spin-echo. In general (i.e., apart from the some specific relations T_1 and T_2) as a result of three 90-degree pulses action, three induction signals arise (after each pulse), and five signals of spin echo (see Sect. 1.8.3). The greatest interest for the relaxation and diffusion measurements are the echo signals (see Fig. 2.37), the maxima which comes at a time $2\tau_1 + \tau_2$ (stimulated echo) and $2\tau_2$ (reflected echo). The dependence of the stimulated echo amplitude on the intervals τ_1 and τ_2 is given by:

$$\exp\left(-\frac{2\tau_1}{T_2} - \frac{\tau_2}{T_1}\right) \exp\left[-\gamma^2 G_0^2 D \left(\frac{2}{3}\tau_1^3 + \tau_1^2\tau_2\right)\right], \quad (2.43)$$

where the first factor describes the relaxation contribution, and the second—the contribution of diffusion to the attenuation of the echo. Obviously, making τ_1 enough small, we can reduce the dependence of (2.43) to the expression:

$$\exp(-2\tau_1/T_2 - \tau_2/T_1).$$

If at a constant τ_1 one varies only τ_2 , then the signal decrease is determined by the dependence $\exp(-\tau_2/T_1)$, and this opens the possibility of measuring the longitudinal (spin-lattice) relaxation time. This method can be recommended if the transient

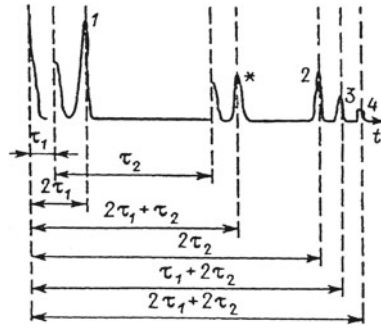


Fig. 2.37 The time diagram of NMR signals in the case of three RF pulse sequence

process in the receiver hinders the observation of free induction signal immediately after RF pulses. On the other hand, the stimulated echo expands possibilities of the spin echo method for measuring the diffusion, since the expression depending on the diffusion includes the product $\tau_1^2 \tau_2$, which can be made large by τ_2 with small τ_1 , that essential in the case $T_2 \ll T_1$.

2.8 Processing of Information by Means of Spin Echo

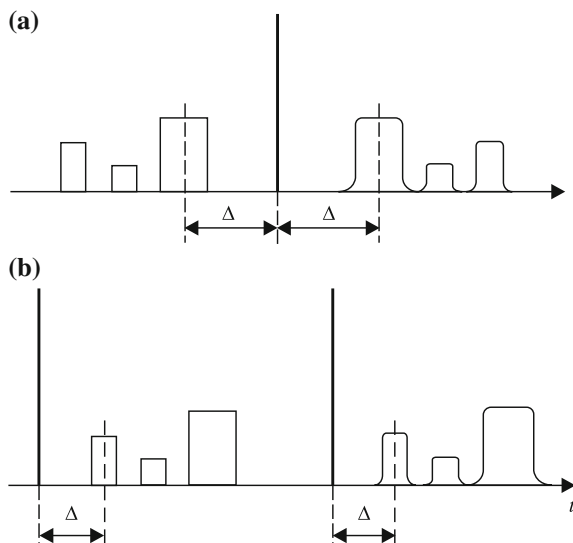
From the material of Sect. 2.5 it follows that the phenomenon of spin-echo can be used for delay and operational memory of signals. Indeed, assuming in a simple two-pulse technique the first pulse as informational and the second as control (or reader), we find that settling the interval between pulses it is possible to cause the signal (echo) in the required time. In this case the only necessary restriction is the condition

$$T_2^* \ll T < T_2,$$

where T is the time of the desirable appearance of the echo signal. The left side of the inequality defines the minimum delay between pulses for the appearance of the echo and the right one restricts the time of an experiment. Thus, the spin system operates as a storage device. Such devices, used spin echo signals, is called *spin processors*.

The cases of particular interest are when the informational pulse is weak (weak-signal approximation). Then the spin system “works” in the linear regime with respect to the information signal and the spin echo reproduces its shape (but like in a mirror, i. e. images are in the reverse order, see Fig. 2.38a). Naturally, instead of a single informational pulse one can apply a few “weak” pulses. For the direct (not inverted) sequence of signals in time the diagram, which is shown in Fig. 2.38b, can be applied. In this case, we use two strong pulses, and the formation of echo signal is the same as the formation of the stimulated echo (see Sect. 2.7).

Fig. 2.38 The scheme of spin-echoes as a random access memory for the inverted (a) and direct (b) order of information



The first communications about possibilities of such use of the spin-echoes are contained in the works of E. L. Hahn with colleagues which were published in 50-ties. In particular, they showed that for the realization of the weak-signal approximation it was necessary to fulfil the following conditions:

(1) the angle of rotation of the vector of nuclear magnetization under the influence informational pulse (signal) must be weak, i. e. $\gamma B_1 t \ll 1$;

(2) the spectrum of the informational pulse (Δf) must be less than the line width of the NMR spectrum, that is equivalent to the condition $\Delta f \ll (1/T_2^*)$, and therefore pulse excites only a small portion of the spins;

(3) the spectrum of the control pulse must be considerably wider the spectrum of the information signal;

(4) the duration of the informational pulse must be much smaller than the spin-spin relaxation time T_2 .

Under these conditions the echo signal at the output of the processor spin retains all the amplitude-frequency correlation of the input signal. These requirements are easily satisfied by the spin-echo technique with registration of nuclear magnetic resonance in magnetically ordered materials (see Chap. 7). This technique provides obtaining sufficiently intensive signals using compact devices (in this case the nuclear magnetic resonance is observed in internal magnetic fields without of magnets). Therefore hereinafter we assume that practical realizations of the described methods of information processing are based on the nuclear magnetic resonance in magnetically ordered substances.

Processing of amplitude-frequency modulated signals using spin processors consists of addressed signal delay, delay a signal without distortion of its shape, frequency filtering, integration, and differentiation of functions. The phenomenon of

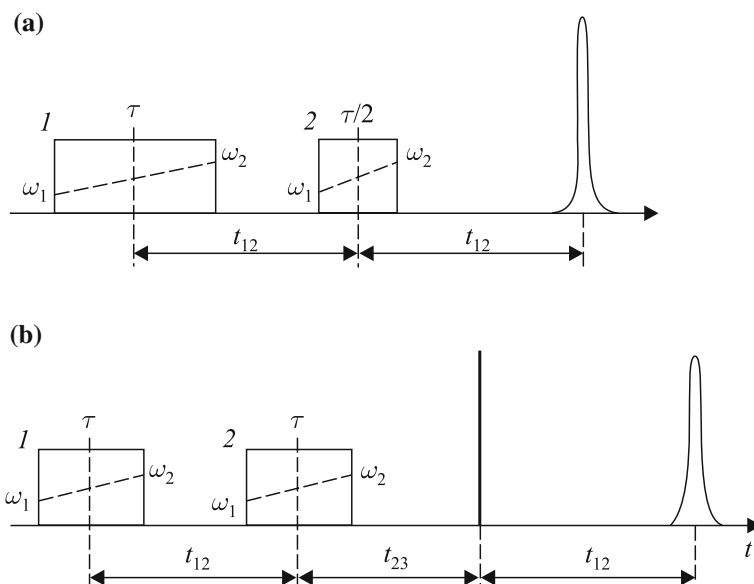


Fig. 2.39 The scheme of the “compressed” spin-echo without (a) and with “strong” pulse (b)

spin-echo can be used for matched filtering or compression of pulses with frequency modulation. In the case of the compression, the energy of a pulse of duration τ is concentrated in a time interval τ/K (K is the compression ratio, $K \gg 1$). Figure 2.39a presents the diagram of the pulse sequence, which consists of an informational pulse (1) and control pulse (2) with linear frequency modulation. The control pulse (2) is in two times shorter than informational one (1) but the change of frequency in both cases occurs in the same range: from ω_1 to ω_2 . Readers are invited to explain the mechanism of the formation of the compressed echo (as an exercise) but it is evident that another coding of pulses does not yield the compressed echo. In the compression mode with two control pulses, one of which is short (δ -pulse with a wide spectrum), an informational signal can be supplied at the first, second or third place in a row (in Fig. 2.39b shows one of the options).

2.9 Radiation Damping: The Interaction of Precessing Nuclear Macroscopic Magnetization with Radio-Frequency Circuit

So far, the behavior of nuclear macroscopic magnetization was considered without taking into account the possible reverse effect of the recording equipment on it.

The main element of the radiospectrometer of nuclear magnetic resonance is the inductor (coil) which is included in the resonant circuit tuned on the frequency of the precession of the vector nuclear macroscopic magnetization $\vec{M}$. The e.m.f.

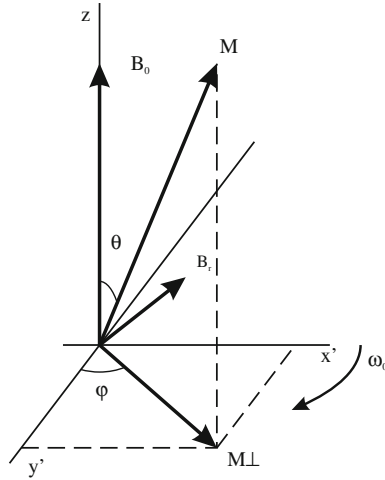


Fig. 2.40 The vector $\vec{M}$ in rotating frame

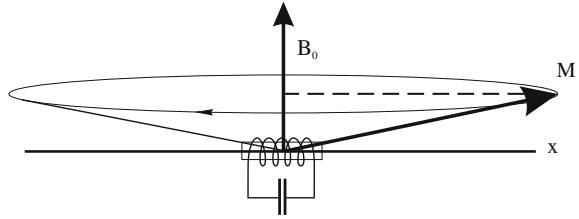
is induced in this inductor according to the formulas (2.15) and (2.16), that leads to an alternating voltage at its ends with an amplitude given by (2.17). Naturally, the alternating voltage creates an electric current in the coil, which generates an alternating magnetic field of $\vec{B}_r$ at the resonance frequency ν_0 . According to the laws of electromagnetic induction, this field lags in phase on 90° from the direction of the transverse components of the vector $\vec{M}$. The physical picture of the rise of the secondary field $\vec{B}_r$ can be illustrated in Fig. 2.40, which shows the corresponding vectors in a rotating with angular frequency ω_0 coordinate system. The amplitude of the field $\vec{B}_r$ is proportional to the transverse component of the vector $\vec{M}$:

$$B_r = kM \sin \theta, \quad (2.44)$$

where k is the proportionality constant that depends on the parameters of the resonant circuit of the NMR signal sensor.

It is obvious that the emerged field $\vec{B}_r$ will affect the nuclear magnetization as well as any external alternating field with the only difference that its value depends on the orientation of $\vec{M}$. According to Fig. 2.40 under the influence of the field $\vec{B}_r$ the vector $\vec{M}$ will rotate around it in the clockwise direction and, as a result, the nuclear magnetization vector is set along the vector field $\vec{B}_0$. It is easy to check that for any initial orientation of the vector $\vec{M}$ in the space the described process develops in this way. It is worth to be emphasized that for the rise of the field $\vec{B}_r$ is connected with the existence of the circulating transverse component of the magnetization $\vec{M}_\perp$, i. e. the effect is absent for the exact orientation of the vector $\vec{M}$ along or against the vector field $\vec{B}_0$. However, as already mentioned, all experiments in the nuclear magnetic resonance are based on the registration of namely circulating transverse components of macroscopic nuclear magnetization.

Fig. 2.41 The RF coil and the precession of the nuclear magnetization around the static magnetic field



Thus, the change in the orientation of the vector $\vec{M}$ in our case is determined by the interaction of the nuclear magnetization with a receiver circuit. Therefore, this effect is called *reaction of resonant circuit*. The Bloch equations (1.56) are insufficient to describe the effect because they do not take into account the existence of the secondary field $\vec{B}_r$, i.e. instead of three variables M_x, M_y, M_z now we have to deal with four ones: M_x, M_y, M_z and B_r . Therefore, it is necessary to complete the Bloch equations by one more equation relating the field $\vec{B}_r$ and the transverse component of the vector $\vec{M}$.

Let the receiving coil is oriented along the axis x of the laboratory system coordinates (Fig. 2.41). Then the e.m.f. will be induced only because of oscillations of the component M_x . From Eqs. (1.59) and (1.60), taking into account (1.68) and (1.69) one can obtain $M_x = -v \sin \omega_0 t$, since $u = 0$ for $\omega = \omega_0$. Then, repeating the calculations in Sect. 2.4, we obtain for the e.m.f. in the receiving coil:

$$E = 4\pi n S \omega_0 v \cos \omega_0 t. \quad (2.45)$$

Voltage u_s on the inductor included in the resonant circuit is more than E in Q times (Q is the quality of the circuit) and its phase is shifted on 90° with respect to the e.m.f.:

$$u_s = 4\pi n S \omega_0 Q v \sin \omega_0 t. \quad (2.46)$$

Taking into account the wellknown relation between the current i and the voltage u on an inductor L : $i = -L^{-1} \int u dt$ one can obtain using (2.46)

$$i = 4\pi n S L^{-1} Q v \cos \omega_0 t.$$

For simplicity we assume that the receiving coil on a design is similar to a long solenoid (i. e., its length is much larger than its diameter). Then

$$B_x \simeq 4\pi n_0 i = (4\pi)^2 n n_0 S L^{-1} Q v \cos \omega_0 t, \quad (2.47)$$

where n_0 is the number of turns per 1 cm. The inductance of a coil is given by $L = 4\pi n^2 S l^{-1}$, where l is the length of the coil, and we finally obtain

$$B_x = -\frac{4\pi Q}{\omega_0} \frac{dM_x}{dt}, \quad (2.48)$$

because

$$\frac{dM_x}{dt} = -\omega_0 v \cos \omega_0 t.$$

Strictly speaking, formula (2.48) should contain the attenuation coefficient η , which takes into account the incomplete filling of the receiving coil by a sample and the finite size of that coil (i.e., the field B_x less than given by (2.47) and (2.48)). The coefficient η can be calculated for each case but for the average experimental conditions it amounts to about 0.3.

Thus, the system of equations for the components of the nuclear magnetization in the laboratory coordinate system is now supplemented by the Eq. (2.48):

$$\begin{aligned} \frac{dM_x}{dt} &= \gamma M_y B_z - \gamma M_z B_y - \frac{M_x}{T_2}, \\ \frac{dM_y}{dt} &= \gamma M_z B_x - \gamma M_x B_z - \frac{M_y}{T_2}, \\ \frac{dM_z}{dt} &= \gamma M_x B_y - \gamma M_y B_x - \frac{M_z - M_0}{T_1}, \\ B_x &= -\frac{4\pi Q\eta}{\omega_0} \frac{dM_x}{dt}. \end{aligned} \quad (2.49)$$

It is impossible to find the general analytical solution of the system of nonlinear Eq. (2.49), however, there are a number of solutions for particular cases. To clarify the basic features of the phenomenon, consider the approximation assuming infinitely large relaxation times T_1 and $T_2(T_2^*)$, when the only reason of the damping of the precession of the vector $\vec{M}$ is the energy transfer to the receiver circuit. In this case the magnitude of the nuclear magnetization remains unchanged, and the angle θ between the vectors $\vec{M}$ and $\vec{B}_0$ gradually decreases (see Fig. 2.40). To describe the behavior of the vector $\vec{M}$ it is enough to use the last two equations in (2.49). Let us write the components of the nuclear magnetization in a spherical coordinate system and substitute the expression for B_x in the third equation of (2.49):

$$\begin{aligned} -M \sin \theta \frac{d\theta}{dt} &= -\gamma M \sin \theta \cos \omega_0 t \left(-\frac{4\pi Q\eta}{\omega_0} \right) M \\ &\times \left[\cos \theta \frac{d\theta}{dt} \sin \omega_0 t + \omega_0 \sin \theta \cos \omega_0 t \right]. \end{aligned}$$

Since the change in of the angle θ can not be fast because of the small amplitude of the field B_x , the first term in square brackets can be neglected ($d\theta/dt \ll \omega_0$). Making the necessary reductions, we obtain

$$\begin{aligned}\frac{d\theta}{dt} &= -4\pi\gamma MQ\eta \sin\theta \cos^2\omega_0 t \\ &= -4\pi\gamma MQ \sin\theta \left[\frac{1}{2} + \frac{1}{2} \cos 2\omega_0 t \right].\end{aligned}\quad (2.50)$$

We are interested in the change of angle θ in the time intervals, significantly exceeding the period of the nuclear magnetization precession. Then the influence of the second term in square brackets in (2.50) can be neglected, since its inclusion would only lead to very small fast changes in of the angle θ with frequency $2\omega_0$. Finally, we obtain:

$$\frac{d\theta}{\sin\theta} = -\frac{dt}{\tau_R}, \quad (2.51)$$

where

$$\tau_R = \frac{1}{2\pi\gamma MQ\eta}. \quad (2.52)$$

The solution of (2.51) is easily obtained if it is converted to a form

$$\frac{d\theta}{\sin\theta} = \frac{d(\tan \frac{\theta}{2})}{\tan \frac{\theta}{2}} = -\frac{dt}{\tau_R}.$$

Then

$$\tan \frac{\theta}{2} = C e^{-t/\tau_R} = e^{(t_0-t)/\tau_R}, \quad (2.53)$$

where C and t_0 are the constants, and t_0 is the point in time when $\theta = \pi/2$.

The purpose of this consideration is to describe the behavior of the transverse relative field $\vec{B}_0$ components of the nuclear magnetization $M_\perp$, which recorded in NMR experiments. Taking into account that

$$M_\perp = M \sin\theta,$$

and expressing $\sin\theta$ with the help of (2.53), we obtain

$$\begin{aligned}M_\perp &= M \frac{2}{(\tan \frac{\theta}{2})^{-1} + \tan \frac{\theta}{2}} \\ &= M \frac{2}{e^{-(t_0-t)/\tau_R} + e^{(t_0-t)/\tau_R}} = M \sinh \frac{t-t_0}{\tau_R}.\end{aligned}\quad (2.54)$$

The function (2.54) for different initial conditions is presented in Fig. 2.42.

Thus, the behavior of the transverse component does not have the character of a damped exponent, as in the case of relaxation, and is described by a more complex function. However, at small values of $\theta(0)$, when $\exp[-(t_0 - t)/\tau_R] \ll 1$ Eq. (2.54) becomes

Fig. 2.42 The behavior of $M_{\perp}$ at different initial conditions

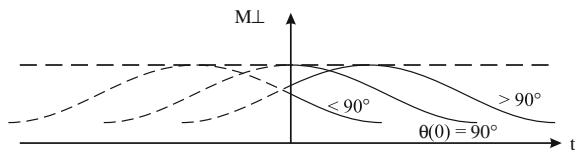
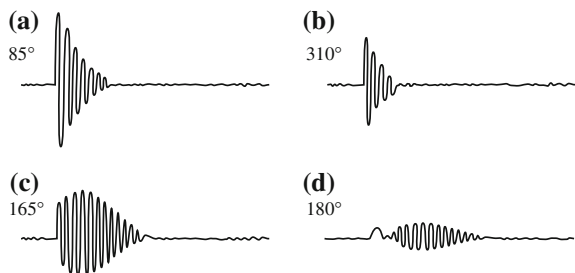


Fig. 2.43 The free induction decay signals of the ^1H nuclei after a single pulse at various angles of the nutation of the nuclear magnetization (to the left of each signal the initial meaning of $\theta(0)$ is indicated): 85° (a); 310° (b); 165° (c); 180° (d)



$$M_{\perp} = M(0)e^{-t/\tau_R},$$

i. e. value of τ_R , defined by (2.52), takes the sense of a damping constant. Mainly because of this, the discussed process is also called *radiation damping*.

This analysis gives the correct description of the effect of radiation damping in the case of relatively high values T_1 and T_2^* , that is confirmed by direct experiments. The free induction decay signals of the ^1H nuclei after a single pulse at various angles of the nutation of the nuclear magnetization are presented in Fig. 2.43 (to the left of each signal the initial meaning of $\theta(0)$ is indicated). It is obvious that the view of the signals is in accordance with the function (2.54) and Fig. 2.42. In these experiments, the the signals were registered with $T_2^* \simeq 2$ s and $\tau_R \simeq 0.3$ s.

An interesting feature of the effect is the possibility of self-excitation (see two last traces in Fig. 2.43) in two coupled resonance systems (nuclear magnetization — rf circuit). If the magnetization is directed in the opposite direction in respect to the vector field $\vec{B}_0$ (it is possible, for example, in the case of the Overhauser effect, See Chap. 16) and $\tau_R \ll T_2^*$, so-called *radiation instability* arises. On the basis of this effect a NMR generator was even created, which completely correspond to masers (see, Chap. 18).

In conclusion, it is worth noting that the additional damping of the transverse component of the nuclear magnetization leads to the broadening of spectral lines. This, in its turn, results in the deterioration of resolution of a radiospectrometer, that one should take into account in the high resolution spectroscopy. Of course, if there are many lines in a spectrum this the effect is less noticeable, because the magnetization of each line precesses at its own frequency, i. e. for the estimation of possible influence of the radiation damping using the formula (2.52) one must substitute a “partial” magnetization M_i for each spectral line with $\sum M_i = M$.

In spite of the main works, in which the radiation damping was discussed, published in the 50–60-ties, the interest to this problem keeps till now.

2.10 Magnetic Resonance Imaging

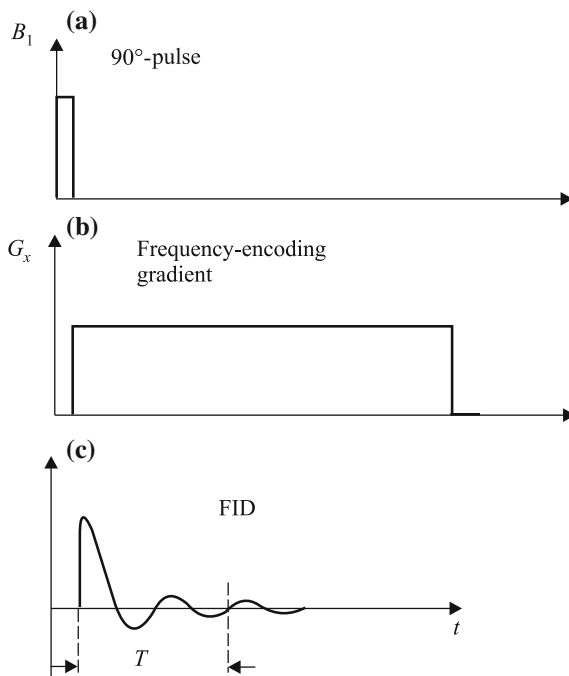
The term *magnetic resonance imaging* (MRI), or else *magnetic resonance tomography*, involves a lot of techniques to get the image in a certain section of the spatial distribution of any characteristic of an object to which the magnetic resonance is sensitive. In a broader sense, the magnetic resonance imaging means getting any localized information using magnetic resonance.

The idea to obtain localized nuclear magnetic resonance spectra and images with NMR was proposed a long time ago (Ivanov V. A. The method of determining the internal structure of objects. Auth. Certificate USSR, No 1112266. Priority from 21.03.60. Bulletin of discoveries and inventions. 1984. No 33. P. 125), but the first publication of the implementation of the method based on nuclear magnetic resonance appeared only in 1973. Shortly after this EPR images were obtained too. EPR imaging is still used as a laboratory research method (for example, to obtain information about the spatial distribution of free radicals), whereas NMR imaging (NMRI) for a long time went out beyond laboratories and it is widely used first of all for the purpose of medical diagnosis. Furthermore the NMRI is used in plant and animal physiology, geophysics, chemical technology, food industry etc. Therefore, the physical principles of the localization of magnetic resonance signals will be considered in case of NMR. Let us consider the principles of establishing of the mutual correspondence between the NMR signal and the position of a volume element of an object (voxel) that produces this signal. There are many ways to establish such correspondence, but the basis of all of them is the proportionality between the magnetic resonance frequency and the magnitude of the magnetic field (1.25).

2.10.1 The Obtaining of Spin Images from NMR Induction Signals in Inhomogeneous Field

A common feature of all the methods of localization is that the experiment is performed in an inhomogeneous magnetic field with a specially organized character of inhomogeneity. If we observe a magnetic resonance in an inhomogeneous static magnetic field, different points in space correspond to the different resonance frequencies in an inhomogeneous field, hence space points are mapped by the frequency. However, the mapping because of the topological properties of the magnetic field is not biunique: the same frequency corresponds not to one, but to a lot of points in a space, located on certain surface. To overcome this difficulty the character of inhomogeneity is changed successively in the course of the experiment. The obtained thereby NMR signal from object contains the information on a spatial distribution of some parameter determining this signal, but this information appears in the implicit (encoded) appearance. Process and way of entering such an information in a magnetic resonance signal are termed as spatial encoding. Decoding (deciphering) of a signal is produced by mathematical processing of the acquired data. Depending on the character of actions on spin system in the course of encoding, the visualization of

Fig. 2.44 Diagram of frequency-encoding pulse sequence with FID acquisition: **a** RF pulse; **b** frequency-encoding magnetic field gradient; **c** signal of free induction decay



spatial distribution of various parameters can be mapped, namely: concentrations of nuclei of the certain types or unpaired electrons, magnetic relaxation rates, chemical shifts, molecular diffusion, parameters of a macroscopic motion of a sample etc. The EPR imaging is still typical stationary methods of magnetic resonance detection, but for obtaining NMR images, as well as in modern NMR spectroscopy, almost exclusively the pulse method is used. A variety of methods for producing spin images are divided into two main groups: the first one is *detection of free nuclear induction signal* in a nonuniform magnetic field, the second one is *excitation of nuclear magnetic resonance signals* in such a field.

To understand the essence of the first method of obtaining the spatial information, let us consider a simple experiment. Just after the action of 90-degree pulse (B_1 in Fig. 2.44a), the magnetic field with a constant gradient (G_x in Fig. 2.44b) is created in the region where the explored object is located. In this situation in each volume element termed *voxel*, there is the precession of nuclear magnetization with the frequency spotted by a voxel position, more exactly by value of its coordinate x . The observed signal of the free induction decay signal (FID) from the whole object is the sum of signals from particular voxels in the object volume (Fig. 2.44c). Hence, the Fourier spectrum of this signal with an appropriate choice of the scale represents the distribution of density of resonating spins along the coordinate x . In other words, the frequency spectrum of the signal of the magnetic resonance is the projection of

density distribution of resonating spins on the direction of gradient of a magnetic field.

Now we will give the formal description of the technique of obtaining a projection of spin density spatial distribution from a FID signal. The induction from particular voxel is determined by transversal components of nuclear magnetization u and v in a rotating frame ($u = M_{x'}$ and $v = -M_{y'}$). Their motion is described by the Bloch equations (1.62) and (1.63) under conditions $B_1 = 0$ and $\delta\omega = \gamma \vec{G} \cdot \vec{r}$, where $\vec{G}$ is the vector of gradient of a magnetic field with components G_x, G_y, G_z ; $\vec{r}$ is the radius vector, defining the position of the voxel. The solution of the system (1.62), (1.63) can be presented in the form of a complex function $m_1(\vec{r}, t) = u - iv$:

$$m_1(\vec{r}, t) = m_1(\vec{r}, 0) \exp\left(i\vec{k} \cdot \vec{r} - \frac{t}{T_2}\right), \quad (2.55)$$

here for convenience we introduce the vector

$$\vec{k} = -\gamma \int_0^t \vec{G}(t') dt' \quad (2.56)$$

Besides it is assumed that, in general, the gradient is the function of time; $m_1(\vec{r}, 0)$ is the value of complex transversal magnetization of the voxel at the time $t = 0$ (let us accept, for example, this is the moment just after a pulse of the radio-frequency field directed along an axis x' in the rotating frame). In this case $|m_1(\vec{r}, 0)|$ is proportional to spin density $\rho(\vec{r})$.

For the simplicity we assume that $t < T_2$. Then, according to the above and the Eq. (2.55), the free nuclear induction signal from whole object is expressed, up to a constant factor, by the function $s(t)$ defined by summation on the volume of the sample V :

$$s(t) = \iiint_V \rho(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) dV. \quad (2.57)$$

Here dV is the volume differential. In this example $k_x = -\gamma G_x t$, $k_y = k_z = 0$. Then the signal from the whole sample can be written as

$$s(t) = \int_{x_1}^{x_2} \rho_1(x) \exp(ik_x x) dx \quad (2.58)$$

Here $\rho_1(x) = \iint_{S_x} \rho(\vec{r}) dy dz$ is the projection of density of spins to the axis x , S_x is the section of object at the plane $x = \text{const}$; x_1 and x_2 are the limits of x values between which the object is located. Dependence of the integrand in (2.58) from t is contained in a variable k_x according to (2.56). The signal $s(t)$ could also be regarded as function of k_x too. It is convenient instead of $s(t)$ to enter a new function $s_1(k_x)$

by means of a relation $s\left(-\frac{k_x}{\gamma G_x}\right) = 2\pi s_1(k_x)$. Using this definition and considering $\rho_1(x) = 0$ out of the gap $[x_1, x_2]$, it is possible to present the function $s_1(k_x)$ in the form

$$s_1(k_x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \rho_1(x) \exp(ik_x x) dx. \quad (2.59)$$

Thus, the information on the spatial distribution of spins expressed by function $\rho(x)$ is already contained in the $s(t)$ (or $s_1(k_x)$ that is equivalent) in the implicit (encoded) appearance. This technique of the input of the spatial information in a NMR signal was called *the frequency encoding*. The explicit expression of spatial distribution is easy to find, as expression (2.59) is the inverse Fourier transformation of $\rho_1(x)$. Hence, to get $\rho_1(x)$, it is sufficient to perform the direct Fourier transform of the function $s_1(k_x)$.

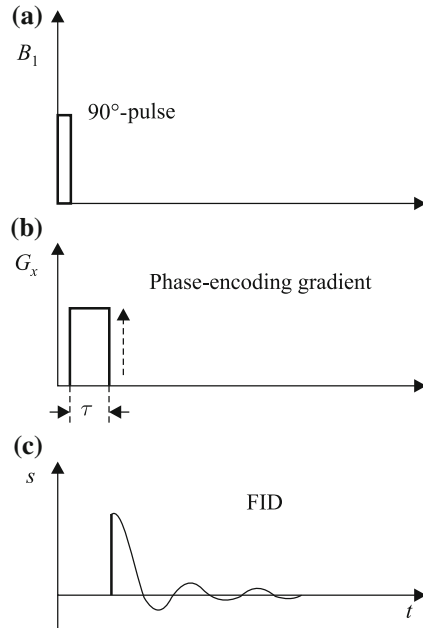
Certainly, in a real experiment the values of function $s(t)$ are measured only in finite number of points N and in a finite interval of time T (See Fig. 2.44c). Values $s(t)$ in these N points form the one-dimensional array of data $\{s_i\}$ to which discrete Fourier transform is applied. One obtains as the result N values ρ_j in the interval

$$-\frac{\pi N}{\gamma G_x T} \div \frac{\pi(N-2)}{\gamma G_x T}.$$

One eliminates a remained uncertainty in two other coordinates with various techniques. Let us confine ourselves to the two possibilities. One of them consists in the frequency encoding which is carried out repeatedly at different directions of a magnetic field gradient. As a result, a set of projections on different directions is obtained. The image of two-dimensional (2D) distribution of density of spins is reconstructed by means of special algorithm (the Radon transformation). Such a technique, termed as *the projection method*, is applied to obtain a pattern of distribution of spin density in certain plane, i.e. *the magnetic resonance tomogram*. The algorithm of reconstruction was applied in other types of a tomography and it does not use the peculiarities of a magnetic resonance, therefore it is not considered here.

Another technique uses so-called *the phase encoding* of a voxel position. For obtaining *an one-dimensional* distribution of density of spins by this technique, the first experiment (Fig. 2.44) should be modify as follows. A gradient pulse is applied after the action of the 90-degree pulse, as above, but the FID signal is registered at fixed moment τ immediately after turning off the gradient G_x (Fig. 2.45b, c). At time τ the precession phase $\phi = \gamma G_x x \tau$ accumulates in every voxel with coordinate x . Thus, the voxel coordinate at the given value G_x is marked by the precession phase at the moment τ . The summed signal from the whole object at the moment τ depends on the distribution function $\rho_1(x)$ and on values G_x . Measurement of the free induction signal is repeated N times at the same interval τ after each following radio-frequency pulse, but each time with a new value of the gradient G_x : $G_{x2}, G_{x3}, \dots, G_{xl}, \dots, G_{xN}$. In Fig. 2.45b the arrow shows conventionally that

Fig. 2.45 Diagram of phase-encoding pulse sequence: **a** RF pulse; **b** phase-encoding gradient; **c** signal of FID free induction decay in homogeneous magnetic field

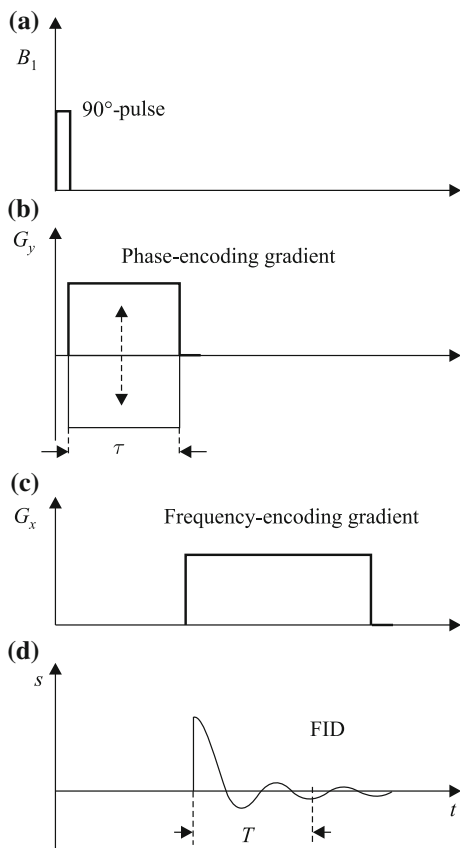


phase-encoding gradient varies at each new measuring. As well as in the previous case, the array $\{s_l\}$ from N values of signals measured at the moment τ (on Fig. 2.45c the vertical segment represents the result of one of measurements) is gotten. Unlike the previous technique, to each value l there corresponds the same value τ , but different values $G_{x,l}$. In this case the variable is not a time, but a gradient. However the form of Eq. (2.59) remains former as it includes only quantity k_x in an explicit form. In this case $k_x = -\gamma G_x \tau$ equally depends on τ and G_x . Hence, a spatial concentration distribution of spins $\rho_1(x)$ is also got by means of Fourier transform. As mentioned above in a real experiment the variable gradient does not change continuously, but takes discrete values. The result of discrete Fourier transform of an array $\{s_l\}$ is the array of values of spin concentration of $\{\rho_m\}$. Each value ρ_m corresponds to a certain value x . The physical difference of this method from the frequency encoding is that the voxel coordinate x is marked not by the frequency of magnetic resonance, but by the difference in phases of the precession which has run at the time τ .

Certainly, excepting some special cases, it is unsuitable to use the phase encoding for obtainment of a two-dimensional image of distribution of spin concentration because in this case the duration of image formation is N times more than at the frequency encoding. Nevertheless, the combination of both methods of encoding allows us to get the two-dimensional spatial information.

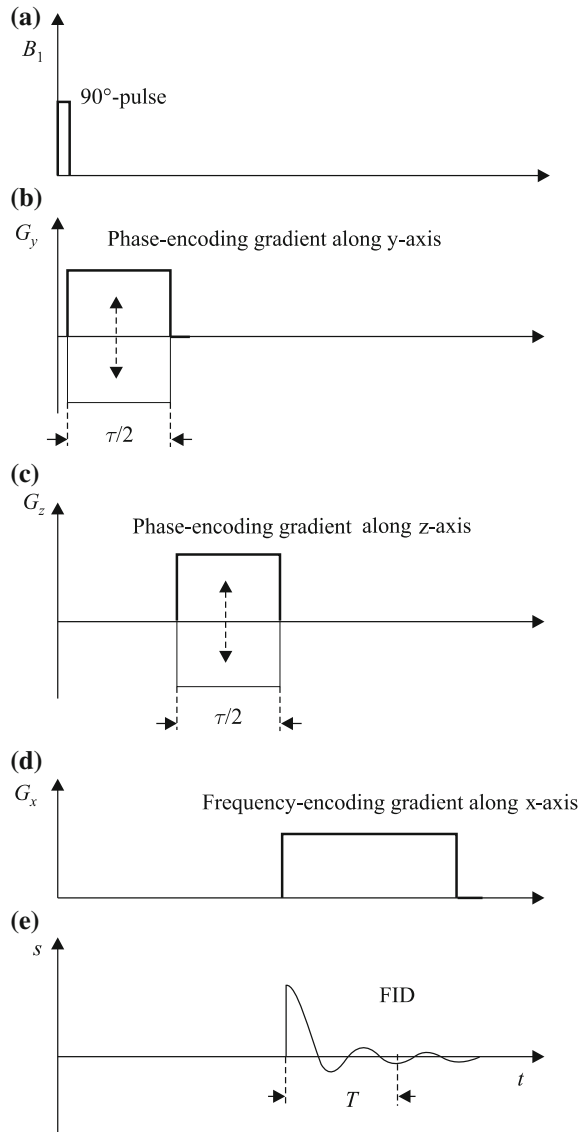
The method of obtaining the two-dimensional image is realized as follows. The transversal nuclear magnetization, as usual, is created by means of a radio-frequency pulse. As well as at obtaining the one-dimensional projection of density

Fig. 2.46 Diagram of pulse sequence for obtaining 2D-image by phase-frequency encoding with FID acquisition: **a** RF pulse; **b** phase-encoding gradient; **c** frequency-encoding gradient; **d** signal of free induction decay



by the method of the frequency encoding, during the registration of FID, the object is in a magnetic field with a constant gradient G_x along the axis x . The difference lies in the fact that the gradient G_x turns on not just after a radio-frequency pulse B_1 (see Fig. 2.46a), but after time τ during of which the magnetic field with a gradient perpendicular to G_x , for example G_y , operates (Fig. 2.46b). At the end of the action of the gradient pulse G_y the magnetization precession for every voxel acquires a phase shift which encodes the position of the voxel along the axis y . This shift determines the initial phase of the precession in every voxel during the action of the frequency encoding gradient G_x (Fig. 2.46c). This experiment is repeated N times with the changing value G_y to provide phase encoding on the coordinate y . Fourier transform of each signal of the free induction (Fig. 2.46d) gives, as result, the spectrum which is a function of x and relates to the certain value G_y . To decode the dependence from y , it is necessary for each value x to execute the second Fourier transform, the integration variable for which is k_y , proportional to G_y . It follows immediately from Eq. (2.57) if to substitute in it $k_x = -\gamma G_x t$, $k_y = -\gamma G_y \tau$, $k_z = 0$. As a result the function of two coordinates (x and y) which represents two-dimensional distribution

Fig. 2.47 Diagram of pulse sequence for obtaining 3D-image by phase-frequency encoding with FID acquisition: **a** RF pulse; **b** the first phase-encoding gradient (along y); **d** the second phase-encoding gradient (along z); **c** frequency-encoding gradient; **e** signal of free induction decay



of spin density in explored object is gained:

$$\rho_2(x, y) = \int_{z_1}^{z_2} \rho(\vec{r}) dz.$$

The above reasoning can easily be extended to three dimensions (the abbreviation 3D-imaging is used). In this case after the action of the 90-degree pulse B_1 (Fig. 2.47a) the phase-encoding gradient G_y operates during the time $\frac{\tau}{2}$ (Fig. 2.47b), and during the following interval $\frac{\tau}{2}$ the phase-encoding gradient G_z (Fig. 2.47c) is applied. Thus for each value of one of phase-encoding gradients, for example G_y , it is necessary to repeat the single experiment N times with the changing value G_z . Thus, on coordinates y and z phase encoding, and on coordinate x a frequency encoding (Fig. 2.47d) are carried out. The formal justification of the method follows immediately from the Eq. 2.57 in which it is necessary to substitute

$$k_x = -\gamma G_x t, \quad k_y = -\frac{\gamma G_y \tau}{2}, \quad k_z = -\frac{\gamma G_z \tau}{2}.$$

In this case the signal of the free induction $s_{G_y G_z}(t)$ depends not only on time, but also on two gradients: G_y and G_z . As well as in the one-dimensional case, instead of $s_{G_y G_z}(t)$ it is more convenient to pass to a function of arguments k_x , k_y and k_z : $s_2(k_x, k_y, k_z)$ or, more compactly, $s_2(\vec{k})$. The required distribution is represented with three-dimensional Fourier transform:

$$\rho(x, y, z) = \int \int \int_{k_x, k_y, k_z} s_2(k_x, k_y, k_z) \exp(-ik_x x) \exp(-ik_y y) \exp(-ik_z z) dk_x dk_y dk_z,$$

that can be written down in more compact form:

$$\rho(\vec{r}) = \int \int \int_{\vec{k}} s_2(\vec{k}) \exp(-i\vec{k} \cdot \vec{r}) d\vec{k}.$$

An advantage of the 3D-imaging is the possibility to reflect a spatial information in an arbitrarily oriented section of an object using a corresponding mathematical processing of the three-dimensional array of data obtained in experiment.

The technique of magnetic resonance imaging reconstruction, which uses multi-dimensional Fourier transform, can be extended to obtain either local NMR spectra, or imaging of a spatial distribution of chemical components of an explored object which are characterized by defined chemical shift. To this purpose an acquisition of FID should be executed, as in usual NMR spectroscopy, in the homogeneous magnetic field, and a phase encoding of all three coordinates should be used. In this case the repetition of a single experiment N^3 times at different values of gradients G_x , G_y and G_z is carried out. It is clear from the above that one has to execute quadruple Fourier transform for the three-dimensional localization of spectra.

2.10.2 Methods of Selective Irradiation

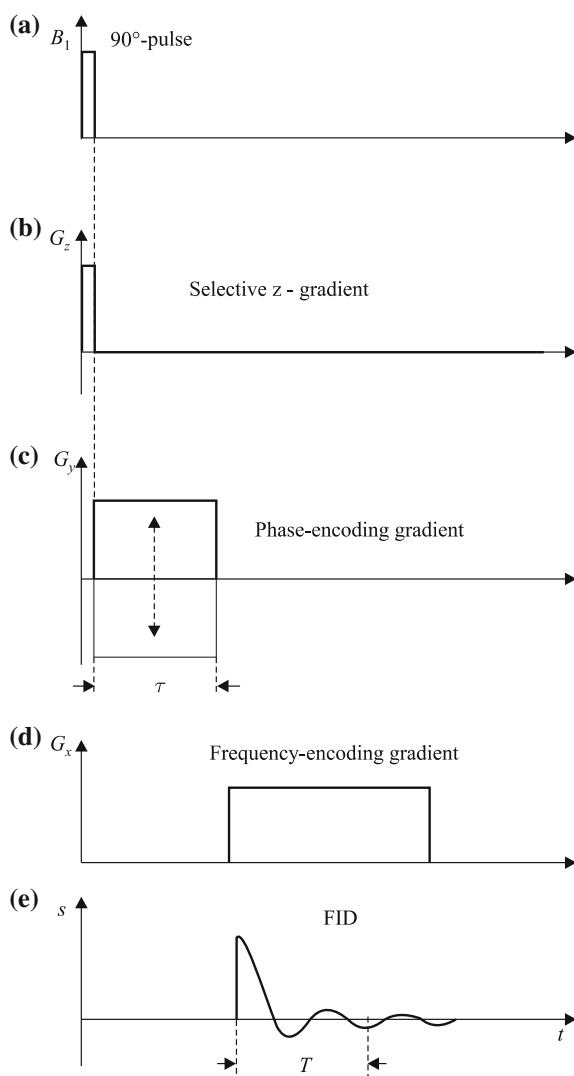
The receiving of data from the whole volume of an object is not always required. For saving of time during data acquisition it is more expedient to excite not all volume, but only an interesting for a researcher part. Practically the matter is about the spatial distribution in certain flat slice from which it is required to get a NMR signal. The problem is solved using *the selective irradiation* idea of which consists in simultaneous action of a radiofrequency pulse and a pulse of gradient, vector of which is perpendicular to the selected slice. It is necessary to choose the width and the shape of the radio-frequency pulse so that the rotation of equilibrium nuclear magnetization on 90 degrees would be carried out only in a narrow frequency band, and consequently, only in the narrow slice adjoining to the plane for which the resonance condition is strictly satisfied. Required parameters of a pulse can be determined by calculation on a base of Bloch equations. It should be noted that the use of Fourier transform is not correct in this case because in the presence of a radio-frequency field the Bloch equations are not linear equations with constant coefficients. Therefore, the superposition principle for their solution is not valid. Nevertheless, in the case of a 90-degree pulse the order of magnitude of a covered frequency band ($\delta\omega$) corresponds to the width of spectrum of a rectangular RF pulse duration t_{sq} :

$$\delta\omega \simeq \frac{1}{t_{sq}}.$$

A combination of the selective irradiation and the 2D-imaging technique allows us to obtain a map of two-dimensional distribution of spin density in the selected slice averaged on its thickness. The diagram of the pulse sequence to realize this, fairly widespread, technique is given in Fig. 2.48. Simultaneously with a RF pulse B_1 (Fig. 2.48a) the magnetic field with a gradient G_z (Fig. 2.48b) acts, thanks to which the RF pulse takes the property of spatial selection. The effects of gradient G_x and G_y (Fig. 2.48c, d) is similar to the described one for the two-dimensional imaging. The peculiarity of the given method is that a signal $s_{G_y}(t)$ (Fig. 2.48e) is received not from the whole object, but only from the selected slice. As a rule, the selective RF pulses are longer and less intensive, than usually applied in NMR spectroscopy, because they are termed *as soft*, unlike broadband, short and intensive *hard* pulses.

For more accurate fixing of boundaries of a slice, instead of square pulses one uses pulses with specially fitted shape. The 2D-imaging in the selected slices requires less time, but spatial resolution along the coordinate which is perpendicular to the selected slice plane is much worse than in the 3D-imaging.

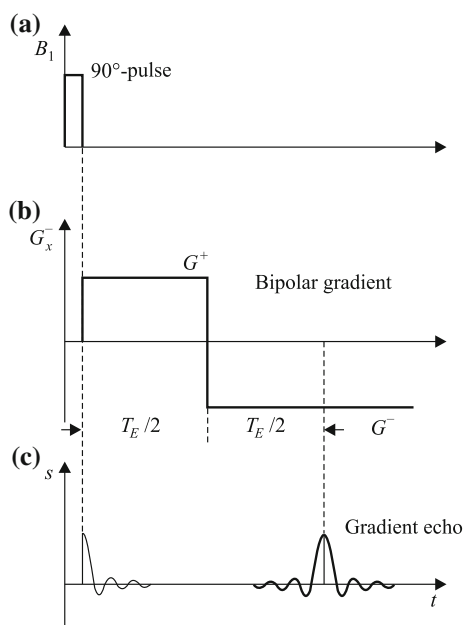
Fig. 2.48 Diagram of pulse sequence for obtaining 2D-image in selected slice by phase-frequency encoding with FID acquisition: **a** RF pulse; **b** selecting gradient; **c** phase-encoding gradient; **d** frequency-encoding gradient; **e** signal of free induction decay



2.10.3 Versions of the Basic Methods of Formation of NMR Imaging

There are various versions of the above basic techniques. One of the most widespread techniques consists in that at a stage of the frequency encoding the signal of spin echo is used instead of free induction.

Fig. 2.49 Pulse diagram for obtaining of a gradient echo.
a RF pulse; **b** bipolar frequency-encoding gradient;
c gradient echo

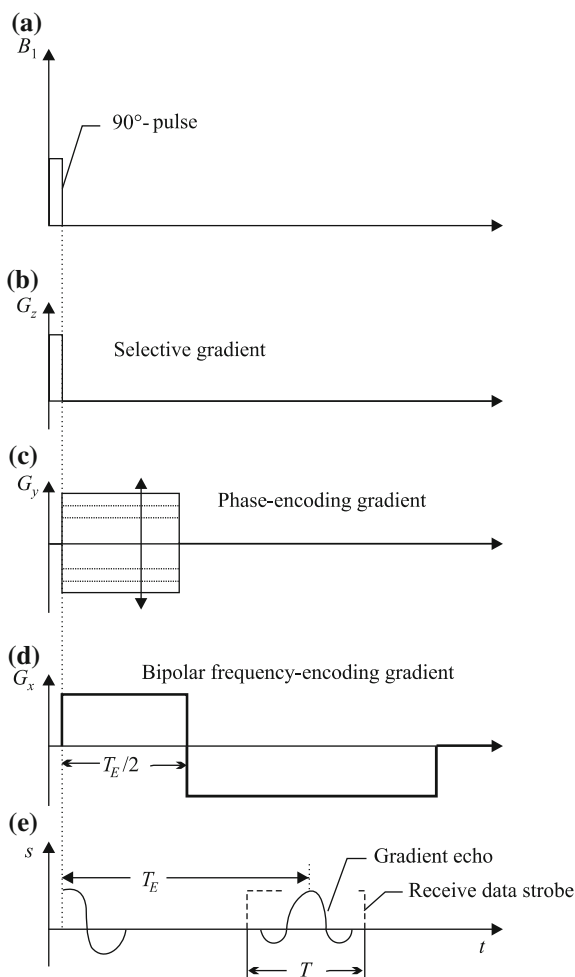


The echo can be created either by introducing an inverting pulse in the certain time interval after the 90-degree pulse (the Hahn echo, see Sect. 2.5.2) or by using of a bipolar gradient (Fig. 2.49).

As an example, the diagram of a pulse sequence for data acquisition for 2D-imaging in the selected slice with bipolar gradient is shown in Fig. 2.50. It is very similar to the diagram in Fig. 2.48, but the gradient which carries out encoding on frequency is made bipolar (G_x in Fig. 2.50d). This leads to appearance of gradient echo with a maximum at the moment T_E after insert G_x ($\frac{T_E}{2}$ is the duration of the positive part: G_x^+) (Fig. 2.50e). The bipolar gradient allows us to get an echo without a 180-degree pulse that removes the problems related to a deviation of its parameters from nominal values. However if Hahn echo decay have a time constant T_2 (a true relaxation time), the time constant of gradient echo decay is T_2^* (an apparent relaxation time), reflecting local inhomogeneity of a magnetic field.

In other widespread updating of the technique, RF pulses, rotating the nuclear magnetization vector by an angle less than 90 degree, are used. In this way, it is possible to reduce considerably the time of data accumulation to construct an image without considerable signal intensity loss. Such a performance uses the fact that the the longitudinal magnetization is proportional to cosine, and the transversal one to sine of the nutation angle. Therefore there is an insignificant deviation from an equilibrium at the small angles that allows the essential reduction of time of equilibrium restoring.

Fig. 2.50 Pulse diagram for obtaining 2D-image in selected slice with gradient echo. **a** RF pulse; **b** selective gradient; **c** phase-encoding gradient; **d** bipolar frequency-encoding gradient; **e** gradient echo



2.10.4 Contrast Enhancement in MRI

The specific feature of magnetic resonance imaging in comparison with other methods of visualization is the possibility to change a local intensity of the received signals in the dependence on various parameters characterizing nuclear magnetic resonance. The change in the appearance of nuclear magnetic resonance images depending on sensitivity to certain parameter is named as parameter contrast. They distinguish so-called *true images* of spatial distribution of a parameter, and *parameter weighted images*. In the first case the values of a parameter as a function of coordinates are calculated from the obtained data and mapped on the display. In the second case, the spatial distribution of transversal magnetization values is mapped. In this case the brightness of image reflects not only the parameter of interest, but also all other

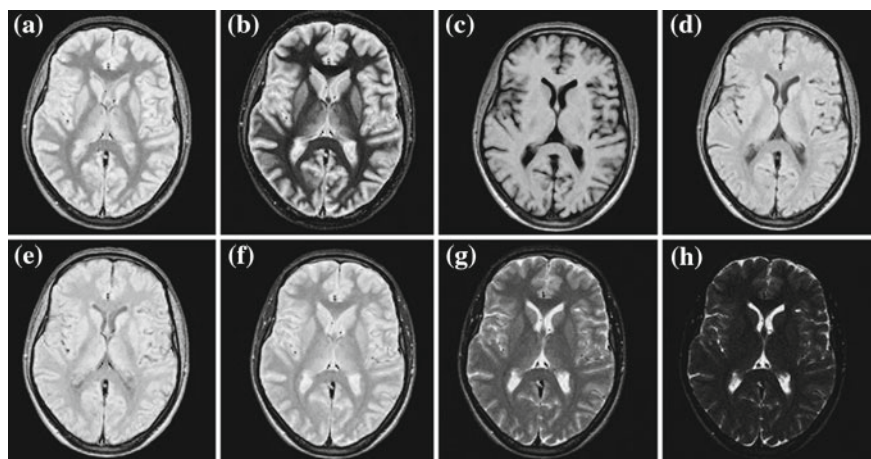


Fig. 2.51 Brain NMR-images by inversion-recovery technique (a–d) and by Hahn spin echo technique (e–h) with repetition time 3400 ms. Time recovery was: a 90 ms; b 200 ms; c 1000 ms; d 2000 ms and time echo was: e 5 ms; f 50 ms; g 120 ms; h 250 ms (The images was kindly provided by Ass. V. Parshina)

factors influencing intensity of NMR signal. Nevertheless, in many applications just the parameter weighted images provide obtaining the necessary information on an object, especially in medical diagnostic. In this cases it is possible to use the simplified techniques that essentially saves a time. Local values of relaxation times, self-diffusion coefficients and quantities characterizing a macroscopic motion of a fluid, magnetization transfer etc can be the parameters to map. Techniques of the obtaining of the true images or parameter weighted ones consist in a combination of standard methods of measurement of corresponding parameters with imaging techniques.

T_1 -relaxation contrast. To obtain local values of T_1 , 180-degree or 90-degree pulse is applied before a 90-degree pulse, as well as in usual time relaxation measurements (see 2.5.1, Fig. 2.30). All other procedures remain the same, as in the case of the imaging of spatial distribution of spin concentration. As a rule, one uses the spin echo with short echo interval T_E to data acquisition instead of FID. The whole cycle of measuring is iterated necessary number of times at different recovery times T_I . For obtaining T_1 -weighted images it is enough to construct the image at one of values T_I , but its optimum value for obtaining the best contrast depends on nature of an explored object. The view of the contrasted image essentially depends on the chosen method and time interval. For example, if one uses the 180-degree pulse (inversion-recovery technique, *IR*), the areas characterized by longer times T_1 , than pulse-to-pulse spacing, and the areas characterized by very short T_1 , can look equally bright, the magnification of brightness is more typical for areas with short times of longitudinal relaxation. Figure 2.51 represents *IR* NMR-images of brain at different recovery times. One can see the very short T_I relative T_1 as well as the very long

(Fig. 2.51a, d) lead to a bad contrast. Intermediate values of T_I give more contrast images (Fig. 2.51b, c). For each kind of tissue the optimal value of T_I exists.

The simplest technique of T_1 -weighting uses standard pulse imaging sequences with the shortened T_R -interval. Then the areas with long T_1 will be reflected with smaller brightness.

T_2 -relaxation contrast. To construct T_2 -weighted images, signals of Hahn echo or echo signals in Carr-Purcell sequence are used (see Sect. 2.5.1). T_2 -weighted image is constructed from signals of Hahn echo with enough long delay of an echo T_E or from enough large number an echo signal in Carr-Purcell sequence (in the last case averaging signal group is often used). Contrary to T_1 -weighted images, T_2 -contrast leads to a reduction of brightness of the areas characterized by small values T_2 (see Fig. 2.51h, where the areas with cerebrospinal fluid are viewed only). At short T_E the contrast is determined only by water content (Fig. 2.51e), and the intermediate T_E -values permit to discriminate between white and gray matter of brain (Fig. 2.51f, g).

T_2^* relaxation contrast. According to aforesaid about the gradient echo, the images constructed under the data from echo measuring at $T_E \geq T_2^*$ reflect a spatial distribution of local inhomogeneities of the magnetic field. These techniques of contrast enhancement are used to map active zones in the cerebral cortex. The method, named the functional magnetic resonance imaging (fMRI) or the blood oxygen level dependent (BOLD) contrast, is based on an effect of augmentation of paramagnetic desoxyhemoglobin in the blood feeding active cortex sites. The fMRI is used to investigate cognitive processing of motion, texture, color, sound, memory etc.

Diffusion contrast. To discriminate areas with different self-diffusion motion of particles containing resonating nuclei on NMR images, as well as in usual measurement of self-diffusion coefficients using NMR, additional magnetic field gradient pulses are introduced into the pulse sequence. It is the most convenient to use a bipolar gradient before a stage of data acquisition. As a result the smaller brightness of an image corresponds to areas with rapid self-diffusion.

Mapping of a macroscopic motion. Manifestations of effects of macroscopic motion of medium within an explored object on NMR images are very manifold and depend on the direction of motion relative the vector of magnetic field gradient and orientation of an imaged plane, the technique of obtaining and processing NMR signals etc. If the motion of medium is perpendicular to the selected slice, saturation of spins in the slice or sounding of nuclear magnetization by the second radio-frequency pulse are used. In the first case the motion leads to magnification of brightness due to inflow of nonsaturated spins, in the second case—to dimness of the image because of ablation of excited spins from the selected slice.

It is widely used so-called *phase contrast* (not to confuse with phase encoding) arising because of NMR frequency change in the voxel moving in the gradient direction. The pulse bipolar gradient is also used, but in this case the positive and negative parts have the equal areas. In case of immobile medium the dephasing of precessions under the influence of the gradient of one sign it is completely compensated by the effect of the gradient of the opposite sign. If there is a motion in the gradient direction then an additional difference in precession phase takes place after a bipolar gradient

pulse. This dephasing leads to the decrease of NMR signal from moving area and, hence, to the decrease in image brightness.

2.10.5 Application of MRI

The basic area of applications of MRI is the medical diagnostics. Expansion and efficiency of the method are determined, first, by the fact that MRI uses intense signal of the protons of water, which is the main component of living systems, and, second, by the variety of parameters that can be visualized in this way.

Relaxation contrast allows us to distinguish the tissues with the identical water content, but having different water states. This is due to the fact that the relaxation is very sensitive to the mobility of water molecules (see Sects. 3.7–3.14). The last, in turn, depends on a type and a biological state of tissue. The contrast-enhanced NMR images are used for early diagnostics of pathological changes of tissues of an organism. In certain cases it is useful to use the self-diffusion contrast enhancement, in particular in the investigation of diffusion anisotropy of brain tissues. Sensitivity of the nuclear magnetic resonance to macroscopical motion in fluids allows us to visualise blood vessels and to estimate their state.

For brain diagnostics, the local spectra of the NMR ^{13}C give an important information. The course of oxidizing processes in muscles can be tracked by means of local spectroscopy ^{31}P . For physiological and cognitive investigations of brain the contrast enhancement by local inhomogeneities of magnetic field inside of a brain is used.

As well as in other methods of visualisation in medicine, the introducing of contrasting reagents in organism is applicable, however the principle of their action is specific for MRI. One uses either the paramagnetic substances providing the strong relaxation contrast, or the ferromagnetic suspensions giving contrast via T_2^* . The prospective technique of molecular visualization uses dynamic polarization (Sects. 15.2, 21.4). In this case the complexes of free radicals or ferromagnetic nanoparticles with biomarkers are used to visualize areas of pathology. In some physiological neurologic experimentes, the possibility of visualisation of trajectories of feeble current is used because of the local inhomogeneities of a magnetic field due to that current.

In non-medical areas of the NMRI, the investigation of porous media are known. The method is based on the possibility of observation of penetration of a liquids in pores and flaws of a solid sample. This direction gave practical results in the investigation of oil-bearing beds. The NMR imaging can be applied as a control device in manufacture of high-quality ceramics at a stage of preparation of ceramic mass, in the course of polymerization of plastic and etc. A special application the NMRI is a monitoring of kinetics of chemical reactions.

An investigation of a spatial distribution of paramagnetic centres, for example, of radiation induced defects and of free radicals, is carried out by the EPR imaging.

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