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Abstract

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"MULTIQUANTUM TRANSITIONS" IN ELECTRON PARAMAGNETIC RESONANCE

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Electron paramagnetic resonance in its usual form is observed in homogeneous magnetic fields: a constant field $\mathbf{H}_0$, which splits the energy levels of the system under study into Zeeman sublevels, and a microwave field $\mathbf{H}_1 \cos\omega_1 t$, perpendicular to $\mathbf{H}_0$, which induces transitions between the latter. In the case where the shell spins of the paramagnetic ion of the sample under study are $S = 1/2$, two Zeeman sublevels are produced, differing in the directions of the projections of the magnetic moment on $\mathbf{H}_0$. Absorption of microwave power will occur at one frequency when the condition is fulfilled

$$\hbar\omega_1 = g\beta H_{01}, \tag{1}$$

where H_{01} is the resonance value of the field H_0 for the frequency ω_1 with which the field H_1 oscillates.

Fig. 1. Scheme of two-quantum transitions

The picture of resonance absorption changes substantially if, in addition to the fields $\mathbf{H}_0$ and $\mathbf{H}_1 \cos\omega_1 t$, another radio-frequency field $\mathbf{H}_2 \cos\omega_2 t$, parallel to $\mathbf{H}_0$, acts on the spin system. With the modern technique of observing EPR, such a situation necessarily occurs: a weak modulating field H_2 with a frequency from the industrial frequency to several kilohertz (video spectroscopes and heterodyne-type spectroscopes) or to several megahertz (spectroscopes with high-frequency modulation) is superposed on the constant field. The influence of the modulating field on the shape of the EPR spectrum has been discussed theoretically and noted experimentally by many authors, especially for the second case, where it is manifested particularly clearly.

A formal treatment of the influence of modulation on the form of the spectrum can be carried out on the basis of general considerations of radio physics ([1]),

Fig. 2. Block diagram of the apparatus

Figure 2: Fig. 2. Block diagram of the apparatus

from which it follows that, for a small modulation index (i.e., when $\Delta\omega/\omega_2 \ll 1$), the spectrum consists of the carrier frequency ω_1 and two sidebands $\omega_1 \pm \omega_2$. In the general case the spectrum represents a set of lines with frequencies $\omega_1 \pm k\omega_2$ of rapidly decreasing intensity. As applied to EPR, an analogous result was obtained ([2]): in the presence of a modulating field H_2, the absorption signal is a series of lines with spacings ω_2 between them and amplitudes proportional to $[J_k(\Delta\omega/\omega_2)]^2$, where J_k is a Bessel function of the first kind.

In recent years several works ([3–6]) have been carried out in which certain features of EPR were observed experimentally with account taken of the influence of the field $H_2 \cos\omega_2 t$; absorption and emission at the frequency ω_2 were discovered. These results were interpreted as the possibility of two-quantum transitions in the spin system. From the viewpoint developed here, the essence of the phenomenon consists in the simultaneous interaction of two photons of different energy and polarization with the system of electron spins, as a result of which absorption and emission arise simultaneously at the two frequencies ω_1 and ω_2 in the fields H_{02} and H_{03}, satisfying the conditions:

$$\hbar\omega_1 + \hbar\omega_2 = g\beta H_{02}, \qquad \hbar\omega_1 - \hbar\omega_2 = g\beta H_{03}. \tag{2}$$

In other words, in the field $H_{02} > H_{01}$ both the quantum $\hbar\omega_1$ and the quantum $\hbar\omega_2$ are absorbed simultaneously (Fig. 1); in the field $H_{03} > H_{01}$ absorption of the quantum $\hbar\omega_1$ and emission of $\hbar\omega_2$ occur simultaneously.

The solution ([4,6]) of the phenomenological Bloch equations for the case under discussion of three fields gives the value of the susceptibility at the frequency ω_2: for $H_0 > H_{01}$ the susceptibility of the paramagnet is positive, which corresponds to absorption of energy at the frequency ω_2, while for $H_0 < H_{01}$ the susceptibility is negative, which corresponds to emission of energy. Despite the undoubted nature of the result set forth, the concept of two-quantum transitions does not seem to us fully substantiated, since the important question of the nature of the intermediate levels of the spin system, without the introduction of which the essence of the phenomenon cannot be understood, remains unexplained. Therefore, the corresponding terminology can for the time being be used only conditionally.

Fig. 2. Block diagram of the apparatus

At the same time, this concept may prove convenient for describing splittings of EPR lines as a result of the modulation effect. We undertook experiments to observe the indicated phenomena in a free radical (diphenylpicrylhydrazyl), using recording both at the frequency ω_1 and at the frequency ω_2. To observe EPR absorption at the frequency ω_1 at room temperature, an ordinary video

Fig. 3. A —action only of the field H1 cos omega1 t; B —action of two fields H1 cos omega1 t and H2 cos omega2 t

Figure 3: Fig. 3. A —action only of the field H1 cos omega1 t; B —action of two fields H1 cos omega1 t and H2 cos omega2 t

spectroscope of the 3-centimeter range was used (Fig. 2), with a resonator operating at the wave H_{011} and with a natural frequency of 9400 MHz. To obtain the field at the frequency ω_2, a coil connected to a GSS-6, GS-23, or IMI-2 generator was installed inside the resonator. The IMI-2 autodyne circuit made it possible to observe absorption and emission signals at the frequency ω_2. The axis of the coil was parallel to the field H_0.

Fig. 3. A —action only of the field $H_1 \cos \omega_1 t$; B —action of two fields $H_1 \cos \omega_1 t$ and $H_2 \cos \omega_2 t$

Figure 3 shows: the absorption signal at the frequency ω_1 and the absorption and emission signals at the frequency ω_2, which arise when the field $H_2 \cos \omega_2 t$ is switched on. At the same time the shape of the signal at the frequency ω_1 changes, which is due to absorption and emission of energy at the frequency ω_2. As already mentioned, with an increase in the modulation index (i.e., with an increase in the amplitude of the field H_2 and with $\omega_2 = \text{const}$) side satellites of the EPR line at the frequencies $\omega_1 \pm k\omega_2$ should arise in increasing number. An attempt was made to observe this effect.

Note: Figure translations are in progress. See original paper for figures.