

Theory of magnetic resonance in the Ising model

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The EPR spectrum (the proper frequencies and the temperature dependences of the line intensities) is calculated for a linear system of spins coupled by Ising exchange interaction. It is shown that, together with the usual magnetic resonance frequency ω_0 , there are also two additional resonance frequencies $\omega_{\pm 1} \equiv \omega_0 \pm J\hbar^{-1}$. Analytic expressions for the line intensities are given for the whole temperature range. An explanation of the experimental data for the EPR signals in the free radical diphenylpicrylhydrazyl is given, and it is shown that the unusual behavior of the line frequency ω_0 at low temperatures can be explained within the framework of the linear Ising model without invoking the idea of a phase transition.

1. INTRODUCTION

In a study of aromatic free radicals by the electron paramagnetic resonance (EPR) method, Prokhorov and Fedorov^[1] established the interesting fact that the EPR signal disappears sharply when the temperature is lowered below a certain point T_m at which the integral intensity of the signal reaches a maximum (cf. also^[2,3]). One of the explanations of this behavior of the integral intensity is that the spin system undergoes a phase transition at the temperature T_m into an ordered (antiferromagnetic) state^[1]. However, structural data^[4] indicate that the exchange-coupled uncompensated spins existing in the free radicals are arranged in the form of chains, the distances between the chains being considerably greater than the distances between the spins within a chain. The assumption of a phase transition requires, in its turn, the assumption of the existence of an appreciable interaction between the chains, since a phase transition is impossible in one-dimensional systems. This, however, is difficult to tie up with the data on the static magnetic susceptibility (χ_0)^[5]. We note, in addition, that attempts to detect antiferromagnetic resonance in the free radical $\alpha\alpha$ -diphenyl- β -picrylhydrazyl (DPPH) at temperatures below the assumed phase transition have not been successful^[6].

In connection with this, the interesting question arises of the choice of a model describing the properties of the free radicals. Linear Ising and Heisenberg models are most often used for this purpose^[5,7]. Such a choice is justified both by the fact that these models reflect well the behavior of exchange-coupled systems, and by the results of structural investigations^[4]. A choice in favor of either of these models can be made only by comparing the predictions of theory with the experimental data. The good agreement between the calculations of χ_0 carried out using the linear Ising model and the experimental data of^[5] indicates that, in a number of cases, an Ising situation exists in aromatic free radicals.

In the present paper we construct a theory of EPR for a system of spins coupled by an exchange interaction of the Ising type, and give a new interpretation of the EPR data, based on a single linear Ising model with no assumption of a phase transition. Since the low-temperature region is of special interest, the theory is developed without using the high-temperature approximation.

In addition to its applications to specific spin systems, the theory developed below, in which a relation is

established between the parameters of the EPR spectrum and the spin correlation functions, shows the possibility in principle of studying collective properties of interacting spin systems by the EPR method.

We note that, although we consider only the one-dimensional Ising model, all the principal results are easily generalized to the case of a model of any dimensionality.

2. MAGNETIC RESONANCE IN THE LINEAR ISING MODEL

To describe the magnetic resonance of a system of spins constituting the Ising model, we shall make use of Kubo's^[8] theory of linear response to the action of an external oscillating field. In this theory, it is usual to subdivide the Hamiltonian of the system being studied into four parts:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_T + \mathcal{H}' + \mathcal{H}'' \quad (1)$$

where the operator \mathcal{H}_0 determines the spectrum of the spin degrees of freedom, \mathcal{H}_T is the Hamiltonian of the remaining degrees of freedom, which constitute the thermostat, and \mathcal{H}' is the operator of the interactions that broaden the spin energy levels and depends, generally speaking, on the variables of the thermostat. The interaction with the oscillating magnetic field $H(t) = H_1 \cos \omega t$, which we take to be directed along the x axis, has the form

$$\mathcal{H}'' = -M_x H(t) = -\hbar \gamma H_x S^x \cos \omega t, \quad S^x = \sum_j S_j^x \quad (2)$$

where S_j^α is the α -component of the spin operator of particle j and γ is the gyromagnetic ratio.

The shape of the EPR spectrum in the approximation linear in the interaction (2) is given by the expression^[8,9]

$$G(\omega) = \frac{\omega}{2E_p(\omega)} \int_{-\infty}^{\infty} \langle M_x(0) M_x(t) \rangle \cos \omega t dt = \sum_{\alpha} A(\omega_{\alpha}) g(\omega - \omega_{\alpha}), \quad (3)$$

$$\{AB\} = 1/2(AB + BA),$$

$$\langle AB(t) \rangle = \text{Sp}(e^{-2\beta \mathcal{H}_0} A e^{i\mathcal{H}_T t/\hbar} B e^{-i\mathcal{H}_T t/\hbar}) / \text{Sp} e^{-2\beta \mathcal{H}_0},$$

$$E_p(\omega) = 1/2 \hbar \omega \text{cth} \beta \hbar \omega, \quad \beta^{-1} = 2kT, \quad M_x = \gamma \hbar S^x.$$

The quantities $A(\omega_{\alpha})$ and $g(\omega - \omega_{\alpha})$ are the intensity and shape function of the resonance line at the proper frequency ω_{α} of the Hamiltonian \mathcal{H}_0 . The widths of the resonance lines will not be considered in this paper, and, therefore, in the Hamiltonian (1) we can put $\mathcal{H}' = 0$ and omit the operator \mathcal{H}_T , which in this case has no effect on the spin variables. For $\mathcal{H}' = 0$, the shape functions

$g(\omega - \omega_\alpha)$ will simply turn out to be equal to $\delta(\omega - \omega_\alpha)$ and will serve only to indicate the proper frequencies.

For the energy operator in the problem, we take the Hamiltonian of the linear Ising model with nearest-neighbor interaction

$$\mathcal{H}_0 = -\hbar\omega_0 \sum_j S_j^z - J \sum_j S_j^x S_{j+1}^x, \quad (4)$$

where ω_0 is the Zeeman frequency and J is the exchange integral between neighboring spins. The case $J > 0$ corresponds to ferromagnetic chains, and the case $J < 0$ to antiferromagnetic chains. We shall expand the operator $S_j^\pm(t) = S_j^X(t) \pm iS_j^Y(t)$, in terms of which the operator $M_X(t)$ is expressed, in a Fourier series in the proper frequencies ω_α of the Hamiltonian (4), equal to $\omega_\epsilon \equiv |\omega_0 + \epsilon\hbar^{-1}|$ ($\epsilon = 0, \pm 1$):

$$S_j^\pm(t) = e^{i\omega_\epsilon t/\hbar} S_j^\pm e^{-i\omega_\epsilon t/\hbar} = \sum_\epsilon S_{j^\pm}(\omega_\epsilon) e^{\mp i\omega_\epsilon t}.$$

Because of the relative simplicity of the Hamiltonian \mathcal{H}_0 , this expansion can be performed exactly. The operators $S_{j^\pm}(\omega_\epsilon)$ can be represented in the following form:

$$S_{j^\pm}(\omega_\epsilon) = R_\epsilon(j) S_{j^\pm}, \quad (5)$$

where the operators $R_\epsilon(j)$ have the form

$$\begin{aligned} R_0(j) &= 1/2(1 - 4S_{j-1}^z S_{j+1}^z), \\ R_{\pm 1}(j) &= 1/4(1 + 4S_{j-1}^z S_{j+1}^z \pm 2S_{j-1}^\pm \pm 2S_{j+1}^\pm). \end{aligned} \quad (6)$$

It is easily verified that the operators $R_\epsilon(j)$ possess the property

$$R_\epsilon(j) R_{\epsilon'}(j) = \delta_{\epsilon, \epsilon'} R_\epsilon(j)$$

and have the meaning of projection operators in the space of the spin states $\Psi\{m_j\} = \prod_j \chi_{m_j}$, where χ_{m_j} is the eigenfunction of the operator S_j^Z , corresponding to the eigenvalue m_j . The operator $R_0(j)$ projects an arbitrary spin state on to the subspace in which the spins $j+1$ and $j-1$ are antiparallel. The operators $R_{\pm 1}(j)$ project spin states on to subspaces in which both spins, $j+1$ and $j-1$, are oriented parallel (+1) and antiparallel (-1) to the direction of the external magnetic field. Substituting the Fourier components (5) into the expression (3), we find the intensities of the resonance lines (calculated per spin)

$$A(\omega_\epsilon) = 1/4 \pi \hbar \gamma^2 \text{th}(\beta \hbar \omega_\epsilon) \langle R_\epsilon(j) \rangle.$$

We note that in spatially uniform systems the expression $\langle R_\epsilon(j) \rangle$ does not depend on j .

The intensity of the EPR line at frequency ω_0 is given by the expression

$$A(\omega_0) = 1/8 \pi \hbar \gamma^2 \text{th}(\beta \hbar \omega_0) [1 - 4 \langle S_{j-1}^z S_{j+1}^z \rangle]. \quad (7)$$

The intensities at the other frequencies are equal to

$$A(\omega_{\pm 1}) = \frac{\pi}{16} \hbar \gamma^2 \text{th}(\beta \hbar \omega_{\pm 1}) [1 + 4 \langle S_{j-1}^z S_{j+1}^z \rangle \pm 4 \langle S_j^\pm \rangle]. \quad (8)$$

For an infinite chain, the spin averages and correlation functions appearing in (7) and (8) have been determined exactly^[10, 11]:

$$\begin{aligned} \langle S_j^\pm \rangle &= 1/2 u \text{sh} \beta \hbar \omega_0, \\ \langle S_{j-1}^z S_{j+1}^z \rangle &= (2 \text{sh} \beta J)^{-2} (\text{ch}^2 \beta J + \text{ch} 2\beta \hbar \omega_0 - uv \text{ch} \beta \hbar \omega_0); \\ u^{-1} &= (\text{sh}^2 \beta \hbar \omega_0 + e^{-2\beta J})^{1/2}, \quad v = \text{ch} 2\beta \hbar \omega_0 + e^{-2\beta J}. \end{aligned} \quad (9)$$

In a paper by Zhelifonov^[11], expressions have also been obtained for $\langle S_j^Z \rangle$ and $\langle S_{j-1}^Z S_{j+1}^Z \rangle$ for a finite chain and for a chain closed into a ring.

Substituting the expressions (9) into (7) and (8), we find

$$A(\omega_0) = \frac{\pi}{2} \hbar \gamma^2 \text{sh}(\beta \hbar \omega_0) e^{-2\beta J} u^2 (2 \text{ch} \beta \hbar \omega_0 + uv)^{-1}, \quad (10)$$

$$\begin{aligned} A(\omega_{\pm 1}) &= \frac{\pi}{16} \hbar \gamma^2 \text{th}(\beta \hbar \omega_{\pm 1}) u^2 (e^{-2\beta J} + e^{\pm 2\beta \hbar \omega_0})^2 \\ &\times (\text{ch} 2\beta J + \text{ch} 2\beta \hbar \omega_0 + u [v \text{ch} \beta \hbar \omega_0 \mp 2 \text{sh} \beta \hbar \omega_0 \text{sh}^2 \beta J])^{-1}. \end{aligned} \quad (11)$$

The expressions (10) and (11) are fairly complicated, and we therefore give simplified formulas below for certain important limiting cases.

Antiferromagnetic Chain ($J = -|J| \equiv -J_0$)

In the high-temperature approximation ($\beta \hbar \omega_0 \ll 1$, $\beta J \ll 1$), the intensities (10) and (11) acquire the form

$$\begin{aligned} A(\omega_0) &= C \omega_0 \left[T + \frac{\Theta^2}{T} \right]^{-1}, \quad A(|\omega_0 \pm J_0 \hbar^{-1}|) = \frac{1/2 C |\omega_0 \pm J_0 \hbar^{-1}|}{T \pm T_N} \\ C &= \frac{\pi \hbar^2 \gamma^2}{16k}, \quad \Theta^2 = \left(\frac{J_0}{4k} \right)^2 + \frac{1}{3} \left(\frac{\hbar \omega_0}{k} \right)^2, \quad T_N = \frac{\hbar \omega_0}{k}, \end{aligned} \quad (12)$$

where the first nonvanishing corrections to the paramagnetic Curie law— $\text{const} \cdot \omega_0/T$ —have been retained. These corrections lead to a law of the Curie-Weiss type only for the resonance lines at the frequencies $|\omega_0 \pm J_0 \hbar^{-1}|$; one of these, $A(|\omega_0 - J_0 \hbar^{-1}|)$, corresponds to the ferromagnetic law, even though we are considering here an antiferromagnetic chain. The role of the Weiss constant in both cases is played by the quantity T_N , which, unexpectedly, has turned out to be unconnected with the exchange interaction and equal to the temperature corresponding to the Zeeman energy.

In the case when the Zeeman energy is considerably less than the thermal energy ($\beta \hbar \omega_0 \ll 1$), we have, in the approximation linear in the field,

$$A(\omega_0) = \frac{\pi}{8} \hbar^2 \gamma^2 \beta \omega_0 \text{ch}^{-1} \frac{\beta J_0}{2}, \quad (13)$$

$$A(|\omega_0 \pm J_0 \hbar^{-1}|) = \frac{\pi}{8} \hbar^2 \gamma^2 \text{th} \frac{\beta J_0}{2} \left[1 \pm \frac{1 - 2e^{-2\beta J_0} \text{ch}^2(\beta J_0/2) \text{sh} \beta J_0}{\text{sh} \beta J_0 \text{ch} \beta J_0} \beta \hbar \omega_0 \right]. \quad (14)$$

Hence we find that, in the absence of the magnetic field ($\omega_0 = 0$), there is one absorption line at the frequency $\omega = J_0 \hbar^{-1}$, with intensity

$$A(J_0 \hbar^{-1}) = \frac{\pi}{4} \hbar^2 \gamma^2 \text{th} \frac{\beta J_0}{2}. \quad (15)$$

It follows from the expression (13) that the intensity $A(\omega_0)$ has a maximum at the temperature $T_m = J_0/2kx$, where x is the root of the equation $x = \coth(x/2)$. Taking into account that $x \approx 1.545$, we obtain the simple formula

$$J_0 \approx 3.09 k T_m \quad (16)$$

for determining the exchange integral in terms of the quantity T_m , which is measured in the experiments of^[1].

In the limit of low temperatures ($\beta \hbar \omega_0 \gg 1$, $\beta J_0 \gg 1$), the behavior of each of the intensities depends essentially on the ratio $p = \hbar \omega_0 / J_0$ of the quantities $\hbar \omega_0$ and J_0 :

$$A(\omega_0) = \begin{cases} 1/2 \pi \hbar \gamma^2 \exp[-2\beta J_0(p-1)], & p > 1, \\ 1/4 \pi \hbar \gamma^2 (3\sqrt{5}-1) (1 - 1/5(3\sqrt{5}-1) \exp(-2\beta J_0)), & p = 1, \\ 1/4 \pi \hbar \gamma^2 \exp[-\beta J_0(1-p)], & p < 1. \end{cases}$$

$$A(|\omega_0 + J_0 \hbar^{-1}|) = \begin{cases} 1/4 \pi \hbar \gamma^2 \exp[-4\beta J_0(p-1)], & p > 1, \\ 1/4 \pi \hbar \gamma^2 (5+2\sqrt{5})^{-1} (1 + 2/5(3-\sqrt{5}) \exp(-2\beta J_0)), & p = 1, \\ 1/4 \pi \hbar \gamma^2 \left\{ 1 - \frac{3}{2} \exp[-\beta J_0(1-p)] \right\}, & p < 1; \end{cases}$$

$$A(|\omega_0 - J_0 \hbar^{-1}|) = \begin{cases} \frac{1}{2} \pi \hbar \gamma^2 \{1 - 4 \exp[-2\beta J_0(p-1)]\}, & p > 1, \\ 0, & p = 1, \\ \frac{1}{2} \pi \hbar \gamma^2 \left\{1 - \frac{5}{2} \exp[-\beta J_0(1-p)]\right\}, & p < 1. \end{cases} \quad (17)$$

Hence it can be seen that as $T \rightarrow 0$ the line $A(\omega_0)$ vanishes (except in the "exotic" case $\omega_0 = J_0 \hbar^{-1}$), and the intensity of the resonance line at the frequency $|\omega_0 - J_0 \hbar^{-1}|$ attains its maximum. In the same limit, the intensity $A(\omega_0 + J_0 \hbar^{-1})$ behaves like $A(\omega_0)$ for $\omega_0 > J_0 \hbar^{-1}$ and like $A(|\omega_0 - J_0 \hbar^{-1}|)$ for $\omega_0 < J_0 \hbar^{-1}$.

Ferromagnetic Chain ($J = |J| \equiv J_0$)

At high temperatures ($\beta \hbar \omega_0 \ll 1$, $\beta J_0 \ll 1$), the intensities (13) and (14) are equal to

$$A(\omega_0) = C \omega_0 \left[T + \frac{\Theta^2}{T} \right]^{-1}, \quad A(|\omega_0 \pm J_0 \hbar^{-1}|) = \frac{1/2 C |\omega_0 \pm J_0 \hbar^{-1}|}{T \mp T_N},$$

where the quantities C , Θ and T_N have the same meanings as in formula (12). Hence it follows that the high-temperature behavior of the line at frequency ω_0 does not depend on whether the chain is ferromagnetic or antiferromagnetic. This means that studying this line in the high-temperature region cannot give information on the nature of the coupling in the chain of spins.

The behavior of the intensities $A(\omega_\epsilon)$ in the case of low temperatures ($\beta \hbar \omega_0 \gg 1$, $\beta J_0 \gg 1$) is given by the expressions

$$A(\omega_0) = \frac{1}{2} \pi \hbar \gamma^2 \exp[-2\beta J_0(p+1)],$$

$$A(\omega_0 + J_0 \hbar^{-1}) = \frac{1}{2} \pi \hbar \gamma^2 \left\{ 1 - \frac{19}{4} \exp[-2\beta J_0(p+1)] \right\},$$

$$A(|\omega_0 - J_0 \hbar^{-1}|) = \begin{cases} \frac{1}{2} \pi \hbar \gamma^2 \exp[-4\beta J_0(p+1)], & p \neq 1, \\ 0, & p = 1. \end{cases}$$

Hence it can be seen that for any values of the parameter p the lines $A(\omega_0)$ and $A(|\omega_0 - J_0 \hbar^{-1}|)$ vanish as $T \rightarrow 0$, and the intensity of the line $A(\omega_0 + J_0 \hbar^{-1})$ tends to its maximum value.

3. DISCUSSION OF THE THEORY AND OF THE RESULTS OF SOME EXPERIMENTS

Figures 1–3 show the characteristic temperature dependences of the intensities of the EPR lines at frequencies ω_0 and $|\omega_0 \pm J_0 \hbar^{-1}|$ for certain values of the parameter p in the cases of antiferromagnetic (the solid lines) and ferromagnetic (the dashed lines) chains. The graphs are given in relative units and on a scale which is indicated on each curve. (Intensities in the same relative units are obtained by multiplying the values taken from the graph by the corresponding scale.)

In Fig. 1, the triangles mark the data of the experiment of Prokhorov and Fedorov^[1] from measurements of the integral intensity of the EPR line in a monocrystalline sample of the free radical DPPH; these data are scaled to the theoretical curve at the maximum. As can be seen from the figure, the data lie well on the curve constructed for the experimental value $p = 0.002$. We note that for $p \ll 1$ the curves $A(\omega_0)$ constructed for the cases $J < 0$ and $J > 0$ coincide within the limits of the accuracy of the figure. This fact means that we cannot determine the sign of the exchange integral. However, its absolute value can be found with high accuracy from formula (16), which is well applicable for the conditions of the experiment of^[1]. Using the experimental value $T_m = 0.30 \pm 0.02^\circ \text{K}$ for the temperature at the maximum, we obtain $J_0 = 0.93 \pm 0.06^\circ \text{K}$. Figure 1 also shows the temperature scale corresponding to this value for the magnitude of the exchange integral.

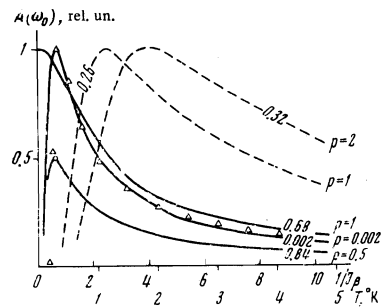


FIG. 1. Temperature dependence of the intensity of the EPR line at frequency ω_0 for the cases of antiferromagnetic coupling (solid curves) and ferromagnetic coupling (dashed curves) for different values of the parameter p . The experimental data (Δ)^[1] and the curve $p = 0.002$ are given on the lower scale.

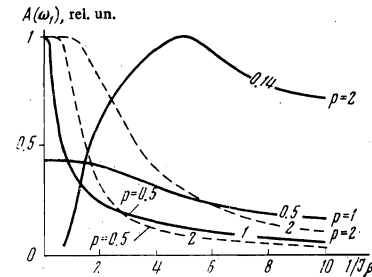


FIG. 2. Temperature dependence of the intensity of the EPR line at frequency $\omega_{+1} = \omega_0 + J_0/\hbar$ for the cases of antiferromagnetic (solid curves) and ferromagnetic (dashed curves) coupling for different values of the parameter p .

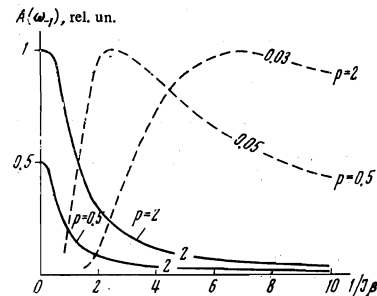


FIG. 3. The same for the EPR line at frequency $\omega_{-1} = |\omega_0 - J_0/\hbar|$.

The fact that an EPR signal is observed in powdered samples of the free radical DPPH at frequency 9600 MHz at temperature 0.25°K ^[7] whereas there is no signal at this temperature at frequency 42 MHz^[1,6] should cause no surprise. This fact is easily explained on the basis of the theory developed, if we assume that the exchange integrals are close in magnitude in the powdered and monocrystalline samples. Then the temperature dependence of the intensity for the experimental conditions in the work of Ruby et al.^[7] ($\hbar \omega_0 / J_0 = 0.49$) is described by the curve with $p = 0.5$ in Fig. 1, which is constructed for the case of antiferromagnetic coupling. The circle on this curve denotes the theoretical intensity value corresponding to the temperature 0.25°K of the experiment. This value differs from zero and lies near the maximum.

The vanishing of EPR signals in other samples of radicals^[2,3] is also described qualitatively by the temperature dependence of the curve $A(\omega_0)$, but a detailed comparison of the theory with experiment is made difficult by the small amount of experimental data.

A conclusion of a general character follows from our results, namely, that a sharp decrease and disappearance of EPR signals is not a sufficient condition for a phase transition. This, incidentally, explains the absence of antiferromagnetic resonance in samples of DPPH in the temperature region below the temperature at which the EPR signal disappears^[6].

To elucidate the physical reasons for the disappearance of the EPR signal, we shall consider configurations of three spins, constituting elements of Ising chains (Fig. 4). The energy absorbed by the spin at the j -th site in the chain in its transitions between the states "along the field" and "against the field" (and, consequently, the resonance frequency) depends essentially on the states in which the spins at the sites $j - 1$ and $j + 1$ are found. The solid arrows in Fig. 4 show the state of the spins before the action of the oscillating field. The dashed arrows show the states into which the spin j goes under the action of the oscillating field. The inverse transition is effected by means of relaxation processes, which are not considered here. For antiferromagnetic coupling, the transitions in the configurations (a) and (b) give absorption lines at the frequencies ω_0 and $\omega_0 + J_0\hbar^{-1}$ respectively. The transitions in the configurations (c) and (d) give the line at the frequency $|\omega_0 - J_0\hbar^{-1}|$.

For $\hbar\omega_0/J_0 \equiv p > 1$, the configurations (d), the number of which increases as $T \rightarrow 0$, are energetically more favorable. The number of configurations (a), (b) and (c) decreases as $T \rightarrow 0$, and this causes disappearance of the lines $A(\omega_0)$ and $A(\omega_0 + J_0\hbar^{-1})$.

For $p < 1$, the configurations (b) and (c) are energetically more favorable. This is the reason for the survival of the lines $A(|\omega_0 \pm J_0\hbar^{-1}|)$ and the disappearance of the line $A(\omega_0)$ as $T \rightarrow 0$.

For $p = 1$ at zero temperature, all configurations are present, and therefore absorption lines exist at all three frequencies.

An analogous explanation can also be given for the resonance lines for a ferromagnetic chain.

The theory predicts the existence of two new EPR lines at frequencies $|\omega_0 \pm J_0\hbar^{-1}|$ in a linear Ising spin system, and also an EPR line at frequency $J_0\hbar^{-1}$ in zero magnetic field. Observation of these lines would make it possible to measure the exchange integral with spectroscopic precision. However, so far as we know, such resonance lines have not yet been observed. A possible explanation of this fact is that the additional lines should lie far from the position expected for free radicals with a g -factor equal to 2, and also that the widths

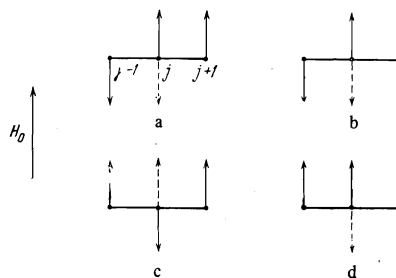


FIG. 4. The spin configurations giving rise to the absorption lines at frequencies ω_0 and $|\omega_0 \pm J_0/\hbar|$.

of these lines are probably much greater than for the ordinary line at frequency ω_0 . In this connection, the problem arises of studying the widths of the resonance lines in the Ising model, especially since we already have interesting data on the temperature dependence of the width of the line $A(\omega_0)$ in the region of the disappearance of the EPR signal, in the paper by Prokhorov and Fedorov^[1].

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