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MULTIQUANTUM ABSORPTION IN A TWO-LEVEL SYSTEM

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A general formula for multiquantum absorption by a two-level system is derived. Multiquantum absorption of the order of k = 2, 3, 4, 5 (k is the number of absorbed photons) has been observed experimentally in the diphenyl picryl hydrazil spin system. The measured dependence of the transition probabilities on the intensity and orientation of the transition-inducing field are in good agreement with results of calculations.

1. INTRODUCTION

MULTIQUANTUM transitions, which consist in simultaneous absorption of two or more photons of equal energy by a particle, were observed many times in the radio-frequency band (see the bibliography in the book of Al'tshuler and Kozyrev [1], and also [2-7]) and in the optical band (see, for example, [8]). The experiments dealt essentially with transitions in which an important role was played by the intermediate levels, and in most cases the distance between the levels was close to the magnitude of the absorbed quanta, so that the effect was appreciable. Less frequently observed were multiquantum transitions without the participation of intermediate levels (absorption in sodium vapor under optical pumping is interpreted in this manner in [5,6]).

In this paper we report the results of an experiment aimed at observing multiquantum transitions (up to fifth order inclusive) between two Zeeman levels of the free radical diphenyl picryl hydrazyl, with the observed photons having equal energy. The theoretical part of the paper contains a derivation of a general formula for the probability of absorption of photons of equal energy by a two-level system, with the interaction between particles taken into account in the derivation. The experimental results are compared with the theory.

2. THEORY

The probability of a process with absorption of k photons and with transition of a particle from the first level to the second is expressed by the formula

$$w_{1\to 2} = R^{-1}\sum_{\alpha}\exp(-E_\alpha/\Theta)\sum_{c_\alpha,\,c_\beta}\left|\langle c_\beta, n-k\,|\,T\,|\,c_\alpha, n\rangle\right|^2, \qquad (1)$$

n—number of photons in the initial state, and the operator T can be represented in the form (see [9]):

$$T = \exp(-i\mathcal{H}_0 t)\left(I + \sum_{m=1}^{\infty} U^{(m)}\right),$$

$$U^{(m)} = (-i)^m \int_0^t dt_m V'(t_m) \int_0^{t_m} dt_{m-1} V'(t_{m-1}) \ldots \int_0^{t_2} dt_1 V'(t_1),$$

$$V'(t) = \exp(i\mathcal{H}_0 t)\, V(t) \exp(-i\mathcal{H}_0 t),$$

$$V = \sum_i (B_i e^{-i\omega t} + B_i^+ e^{i\omega t}). \qquad (2)$$

The term $\mathcal{H}_0$ consists of the unperturbed Hamiltonian and the secular part of the operator W for the interaction between particles, both divided by ħ; V is the interaction between the particles and the external field. The states $|c_\alpha\rangle$ and $|c_\beta\rangle$ are superpositions of states corresponding to the unperturbed values of the energy

$$E_\alpha = N_{1\alpha}a_1 + N_{2\alpha}a_2, \quad E_\beta = (N_{1\alpha}-1)a_1 + (N_{2\alpha}+1)a_2.$$

$N_{1\alpha}$, a_1, and $N_{2\alpha}$, a_2 are the numbers of the particles and the particle energies in the first and second levels; $|c_\alpha\rangle$ and $|c_\beta\rangle$ are eigenvectors of the secular part of the operator W, and the corresponding eigenvalues are denoted by $W(c_\alpha)$ and $W(c_\beta)$; Σ_α in formula (1) denotes summation over all $N_{1\alpha}$ and $N_{2\alpha}$, connected by the relation $N_{1\alpha} + N_{2\alpha} = N$ (N—total number of particles); Θ—product of the Boltzmann constant by the absolute temperature; R—normalization factor:

$$R = \sum_\alpha \frac{N!}{N_{1\alpha}!\,N_{2\alpha}!}e^{-E_\alpha/\Theta} = (e^{-a_1/\Theta} + e^{-a_2/\Theta})^N.$$

When perturbation theory is applicable, we can substitute $U^{(k)}$ in (1) in lieu of T. Inasmuch as $\omega_0 \approx k\omega$, it is sufficient to retain in the expression for the matrix element only the resonant part

$$\langle c_\beta | U^{(k)} | c_\alpha\rangle = \langle c_\beta | M_k | c_\alpha\rangle \int_0^t dt'$$
$$\times \exp\{i[\omega_0 - k\omega - W(c_\alpha) + W(c_\beta)]t'\}, \qquad (3)$$

where M_k—time-independent operator. In formula (3) and in those that follow we shall not write out the photon indices, and we assume that B_i is expressed in terms of the classical field value, since the number of photons n is assumed large. The use of the quantized field is convenient during the first stage of the calculation, since it permits an unambiguous quantum treatment of the effect and, furthermore, makes it possible to discard immediately the terms with photon-production operators.

With the aid of (3) we obtain the following value of the transition probability per unit time:

$$\partial w_{1\to 2} / \partial t = 2\pi G_k(0) g(\omega_0 - k\omega), \qquad (4)$$

$$g(\omega_0 - k\omega) = [2\pi G_k(0)]^{-1}$$
$$\times \int_{-\infty}^{\infty} d\tau \exp\{i(\omega_0 - k\omega)\tau\}\, G_k(\tau), \qquad (5)$$

$$G_k(\tau) = R^{-1} \sum_\alpha \exp(-E_\alpha/\Theta)\, \mathrm{Sp}\, \{P_\alpha M_k^+ P_\beta$$
$$\times \exp(iP_\beta W P_\beta \tau) M_k \exp(-iP_\alpha W P_\alpha \tau)\}, \qquad (6)$$

where P_α and P_β are projection operators.

This expression can be obtained either by representing the square of the modulus of the integral in formula (3) in the form of a δ-function multiplied by $2\pi t$, or else by directly differentiating it with respect to the time. In the latter case the limits of the integral (5) will be $-t$ and t, and the use of the δ-function formalism is equivalent to neglecting the small values of the integral (when t is large) from $-\infty$ to $-t$ and from t to ∞. The function $G_k(\tau)$ is a generalization of the autocorrelation function known from the theory of single-photon transitions (see, for example, [10]), and can be used to obtain the moments of the function $g(\omega_0 - k\omega)$:

$$\overline{(\omega_0 - k\omega)^n} = \frac{i^n}{G_k(0)} \left.\frac{d^n G_k(\tau)}{d\tau^n}\right|_{\tau=0}. \qquad (7)$$

It is not the task of the present paper to investigate the line shape. We note only that with the aid of the obtained general formulas we can show that if we exclude from consideration the possibility of transferring a quantum from one particle to another, and if we can assume the lines to be well resolved, then the function g will be the same for all values of k.

It can be shown that when the total number of photons is large, the function $G'_k(\tau)$, corresponding to the transition 2 → 1 with emission of k quanta, is equal to $N_2 N_1^{-1} G_k(\tau)$ (N_1 and N_2—equilibrium values of the populations). The observed effect is therefore determined by the expression

$$\partial w_{1\to 2} / \partial t - \partial w_{2\to 1} / \partial t = 2\pi$$
$$\times (N_1 - N_2) N_1^{-1} G_k(0) g(\omega_0 - k\omega). \qquad (8)$$

We proceed to calculate the function $G_k(0)$. We shall consider processes in which all k quanta are absorbed by a single particle. In this case there remains in the operator N_k only a single sum of the products of the operators B_i, taken over the numbers of the particles. The value of $G_k(0)$, which is the product of two sums, again reduces to a single sum, since each operator which transfers the particle from state 1 into state 2 should be multiplied by an operator which returns the same particle to state 1. All the interaction operators B_i are assumed identical (we shall henceforth omit the index i), and the calculation of the trace leads only to the appearance of the Boltzmann factor N_1 (for more details on the calculation of traces see [11]).

Thus, the calculation of $G_k(0)$ reduces in practice to the solution of a single-particle problem. (This remark remains in force also for arbitrary processes with transition to another level and with a frequency relation $\Sigma_s k_s \omega_s \approx \omega_0$.)

The function $G_k(0)$ can be represented in the form

$$G_k(0) = N_1 \omega^{2(1-k)} \left| \sum_q f_q D_q \right|^2, \qquad (9)$$

$$D_q = (B_{21})^{q+1} (B_{12})^q (B_{11} - B_{22})^{k-2q-1}. \qquad (10)$$

The summation over q is from zero to the integer part of the number $(k - 1)/2$, while f_q are dimensionless coefficients that are sums of the expressions

$$[b_1(b_1 + b_2) \ldots (b_1 + b_2 + \ldots + b_{k-1})]^{-1}, \qquad (11)$$

corresponding to the combinations of the matrix elements that lead to the product (10); b_p—coefficient of $i\omega t_p$ in the exponential of the time factor of the p-th integral in expression (2). In the calculation of f_q we can assume that $k\omega = \omega_0$.

We use a graphic representation of the products of matrix elements (see, for example, the diagram of Fig. 1a: the points on the lower horizontal line correspond to state 1, the points on the upper line to state 2; the time is directed from left to right; the diagram 1a corresponds to the product $B_{21}B_{12}B_{22}B_{21}B_{11}$). In formula (10) the diagonal elements enter only in the form of the difference $B_{11} - B_{12}$ (this can be verified, for example, with the aid of the equations for the density matrix), so

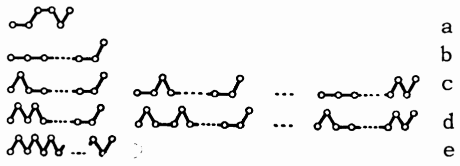

FIG. 1. Graphic representation of the products of matrix elements.

that it is sufficient to consider only diagrams with horizontal segments on the lower level only, and also the sawtooth diagram 1e. From the form of the diagram we determine immediately the coefficient (11). It can be shown that $b_p = -1$ for the horizontal segment $b_p = k - 1$ for the rising segment, and $b_p = -k - 1$ for the descending segment.

With the aid of the diagram 1b we obtain

$$f_0 = (-1)^{k-1} / (k-1)! \tag{12}$$

For the case $q = 1$ (Fig. 1c) we obtain the coefficients

$$\frac{(-1)^{k-1}}{(k-1)!}\frac{-1}{k-1}, \quad \frac{(-1)^{k-1}}{(k-1)!}\frac{-2}{k-2}, \ldots,$$
$$\frac{(-1)^{k-1}}{(k-1)!}\frac{-(k-2)}{k-(k-2)}.$$

Consequently

$$f_1 = \frac{(-1)}{(k-1)!}\sum_{p_1=1}^{k-2}\frac{p_1}{k-p_1}. \tag{13}$$

To calculate f_2 we must consider diagrams with two teeth, which can be obtained from the diagrams 1c by inserting in each diagram, in all possible manners, a second tooth on the right of the first. For example, from the first diagram 1c we obtain the diagrams 1e, which correspond to the coefficients

$$\frac{(-1)^{k-1}}{(k-1)!}\frac{-1}{k-1}\frac{-3}{k-3}\quad \frac{(-1)^{k-1}}{(k-1)!}\frac{-1}{k-1}\frac{-4}{k-4}, \ldots,$$
$$\frac{(-1)^{k-1}}{(k-1)!}\frac{-1}{k-1}\frac{-(k-2)}{k-(k-2)}$$

etc. Continuing this reasoning, we can readily derive a general formula for $q > 0$:

$$f_q = \frac{(-1)^{k+q-1}}{(k-1)!}\sum_{p_1=1}^{k-2}\sum_{p_2=p_1+2}^{k-2}\cdots$$
$$\cdots\sum_{p_q=p_{q-1}+2}^{k-2}\frac{p_1p_2\ldots p_q}{(k-p_1)(k-p_2)\ldots(k-p_q)} \tag{14}$$

Expression (8)—(10), (12), and (14) yield the general solution of the problem.

In the case of dipole interaction, putting $B = -(\frac{1}{4})\gamma\sigma\cdot H_1$ and introducing the angle ϑ between the directions of the constant and alternating magnetic field, we obtain

$$N_1^{-1}G_k(0) = {}^1\!/_4\,\omega^2(\gamma H_1/2\omega)^{2k}[(k-1)!]^{-2}F_k; \tag{15}$$

$$F_1 = \sin^2\vartheta, \qquad F_2 = \sin^2\vartheta\cos^2\vartheta,$$
$$F_3 = \sin^2\vartheta(\cos^2\vartheta - {}^1\!/_8\sin^2\vartheta)^2,$$
$$F_4 = \sin^2\vartheta\cos^2\vartheta(\cos^2\vartheta - {}^1\!/_3\sin^2\vartheta)^2,$$
$$F_5 = \sin^2\vartheta(\cos^4\vartheta - {}^{29}\!/_{48}\sin^2\vartheta\cos^2\vartheta + {}^3\!/_{128}\sin^4\vartheta)^2 \tag{16}$$

etc.

3. EXPERIMENT

In the experiment we used an ordinary magnetic-resonance spectroscope assembled in accordance with the Rollin scheme, using magnetic modulation and synchronous detection at 100 kcs, with the derivative of the absorption line recorded automatically. A rotating magnet made it possible to vary the angle ϑ. The spectroscope generator supplied a voltage up to 100 V to the resonant circuit with the sample.

Figure 2 shows samples of recordings obtained at 12.8 Mcs with different values of H_1. It is seen on Fig. 2 that absorption peaks corresponding to increasingly higher values of k appear with increasing H_1.

The dependence of the amplitudes S_k of these peaks (in arbitrary units) on H_1 for $\vartheta = 30°$ is shown in a logarithmic scale in Fig. 3. The straight lines on Fig. 3 have been drawn with a slope corresponding to a dependence in the form H_1^{2k-1}; this dependence is obtained from (15) if account is taken of the fact that the amplitude of

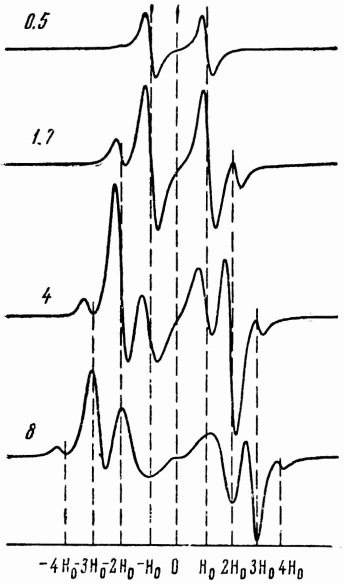

FIG. 2. Derivative of the absorption line at different values of the field intensity H_1 of the field inducing the transitions. The values of H_1 (in Oe) are indicated on the curve: $\omega/2\pi = 12.8$ Mcs, $\vartheta = 45°$.

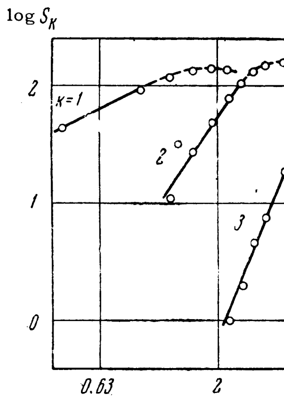

FIG. 3. Dependence of the amplitudes of the absorption peaks S_k on H_1, the straight lines are drawn with slope H_1^{2k-1}.

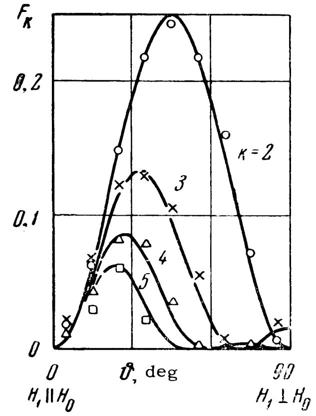

FIG. 4. Solid lines – plots of the functions F_k; the experimental points are normalized independently for each value of k.

the observed signal is proportional to $G_k(0)/H_1$. The deviation of the experimental data from this law at large H_1 is explained by the effect of saturation and superposition of peaks, corresponding to the neighboring values of k.

In Fig. 4 the continuous lines are plots of the functions $F_k(\vartheta)$ (16); the experimental points have been normalized for each value of k independently. We note that the ϑ-dependence of the individual terms in (16) can be interpreted from the point of view of angular-momentum conservation, if we recognize that the component of $\mathbf{H}_1$ parallel to $\mathbf{H}_0$ does not have a momentum relative to the quantization axis, while the photons of the perpendicular component of $\mathbf{H}_1$ can change the momentum of the spin system by $\pm\hbar$ [5,12].

The good agreement between the experimental data and formulas (15) and (16) demonstrates the correctness of treating the supplementary absorption peaks as being the result of multiquantum transitions.

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