FIZIKA 8 (1976) 217—223

FINE PHENOMENA IN ENDOR SPECTRA OF EQUIVALENT NUCLEI

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Received 5 March 1976; revised manuscript received 5 May 1976

Abstract: Exact solution for the eigenvalue problem of the spin Hamiltonian for the unpaired electron and two or three magnetically equivalent protons have been obtained. Besides the splitting of the order of $a^2/(\nu_e + \nu_p)$ in both the upper and lower branch of the ENDOR spectrum, one obtains the differences of the order of $a^3/(\nu_e + \nu_p)^2$ in the splittings of the two branches. Theory demonstrates that for three equivalent protons (rotating methyl group) resonances belonging to the $I = 1/2$ state in the presence of lines belonging to $I = 3/2$ can be detected only from the relative intensities of the observed lines.

1. *Introduction*

In recent years, electron-nuclear double resonance (ENDOR) has been extensively used as a method complementary to electron spin resonance (ESR) in the study of free radicals in organic materials. In such free radicals one often encounters hyperfine interactions of the unpaired electron with two or more equivalent protons. In such cases, a standard first-order perturbation treatment gives equidistant nuclear sublevels which would result in a single transition frequency. The second-order term in the perturbation treatment leads to non-equidistant levels and to more than one transition frequency[1,2].

The case of two methylene protons has been treated by Gloux[3], based on the approximation method developed by Pryce[4]. It reduces the problem to the subspace $S_z = 1/2$ (or to the subspace $S_z = -1/2$), so that one finally has to diagonalize a 4×4 matrix instead of an 8×8 matrix. However, in this paper we show that it is possible to obtain exact solutions for equivalent hyperfine interactions. The exact solution, when compared with the perturbation treatment shows certain differences which will also be discussed.

2. *Two-proton case*

Let us first consider the case of two protons. The spin Hamiltonian of the system containing the unpaired electron and two protons with isotropic hyperfine interactions with the electron can be written in frequency units in the following form

$$\mathscr{H} = \nu_e S_z - \nu_p(I_{1z} + I_{2z}) + a_1 \vec{S}\vec{I}_1 + a_2 \vec{S}\vec{I}_2, \tag{1}$$

where ν_e and ν_p represent the Zeeman splittings of the electron and the protons, respectively, and a_1 and a_2 are the hyperfine splittings.

For $a_1 \neq a_2$, the two protons experience different local magnetic fields. A suitable starting basis for a perturbation treatment consists of the products of the individual spin wavefunctions. For $a_1 = a_2$, the two protons feel the same local magnetic field and the Hamiltonian can be written in terms of the total nuclear spin $\vec{I} = \vec{I}_1 + \vec{I}_2$

$$\mathscr{H} = \nu_e S_z - \nu_p I_z + a\, S_z I_z + \frac{1}{2} a\,(S^+ I^- + S^- I^+). \tag{2}$$

The most suitable starting basis for the perturbation treatment consists of the products of an electronic spin wavefunction $|\alpha_e >$ or $|\,\beta_e >$ and a nuclear triplet spin wavefunction $|T_1 >$, $|\,T_0 >$ or $|\,T_{-1} >$ or the nuclear singlet spin wavefunction $|\,S >$. The eight vectors forming the basis can be designated as $|\,\alpha_e T_1 >$, $|\,\alpha_e T_0 >$, $|\,\alpha_e T_{-1} <$, $|\,\alpha_e\, S >$, $|\,\beta_e T_1 <$, $|\,\beta_e T_0 >$ $|\,\beta_e T_{-1} >$, $|\beta_e S >$. One can easily calculate the matrix element of Hamiltonian (2) in that representation. By suitable ordering of the wave function one obtains the almost diagonal matrix shown in the Table.

The exact solutions of the secular equation are as follows

$$E_{\alpha_e T_1} = \frac{1}{2}\nu_e - \nu_p + \frac{1}{2} a,$$

$$E_{\alpha_e T_0} = -\frac{1}{2}\nu_p - \frac{1}{4} a + \frac{1}{2}\left((\nu_e + \nu_p)^2 + a\,(\nu_e + \nu_p) + \frac{9}{4} a^2\right)^{1/2},$$

$$E_{\alpha_e T_{-1}} = \frac{1}{2}\nu_p - \frac{1}{4} a + \frac{1}{2}\left((\nu_e + \nu_p)^2 - a\,(\nu_e + \nu_p) + \frac{9}{4} a^2\right)^{1/2},$$

Table

	$\mid \alpha_e T_1 >$	$\mid \alpha_e T_0 >$	$\mid \beta_e T_1 >$	$\mid \alpha_e T_{-1} <$	$\mid \beta_e T_0 >$	$\mid \beta_e T_{-1} >$	$\mid \alpha_e S >$	$\mid \beta_e S >$
$< \alpha_e T_1 \mid$	$\frac{1}{2}\nu_e - \nu_p + \frac{1}{2}a$	0	0	0	0	0	0	0
$< \alpha_e \mid T_0 \mid$	0	$\frac{1}{2}\nu_e$	$\frac{\sqrt{2}}{2}a$	0	0	0	0	0
$< \beta_e T_1 \mid$	0	$\frac{\sqrt{2}}{2}a$	$-\frac{1}{2}\nu_e - \nu_p - \frac{1}{2}a$	0	0	0	0	0
$< \alpha_e T_{-1} \mid$	0	0	0	$-\frac{1}{2}\nu_e - \nu_p - \frac{1}{2}a$	$\frac{\sqrt{2}}{2}a$	0	0	0
$< \beta_e T_0 \mid$	0	0	0	$\frac{\sqrt{2}}{2}a$	$-\frac{1}{2}\nu_e$	0	0	0
$< \beta_e T_{-1} \mid$	0	0	0	0	0	$-\frac{1}{2}\nu_e + \nu_p + \frac{1}{2}a$	0	0
$< \alpha_e S \mid$	0	0	0	0	0	0	$\frac{1}{2}\nu_e$	0
$< \beta_e S \mid$	0	0	0	0	0	0		$-\frac{1}{2}\nu_e$

$$E_{\alpha_e S} = \frac{1}{2}\nu_e, \tag{3}$$

$$E_{\beta_e T_1} = -\frac{1}{2}\nu_p - \frac{1}{4}a - \frac{1}{2}\left((\nu_e + \nu_p)^2 + a(\nu_e + \nu_p) + \frac{9}{4}a^2\right)^{1/2},$$

$$E_{\beta_e T_0} = \frac{1}{2}\nu_p - \frac{1}{4}a - \frac{1}{2}\left((\nu_e + \nu_p)^2 - a(\nu_e + \nu_p) + \frac{9}{4}a^2\right)^{1/2},$$

$$E_{\beta_e T_{-1}} = -\frac{1}{2}\nu_e + \nu_p + \frac{1}{2}a,$$

$$E_{\beta_e S} = -\frac{1}{2}\nu_e.$$

By expanding the square roots in a power series in $a/(\nu_e + \nu_p)$, we can approximate the exact solutions to a desired degree of precision. The second-order term gives the splitting of $a^2/2(\nu_e + \nu_p)$ both in the $S_z = 1/2$ and $S_z = -1/2$ branches. For a $\cong$ 100 MHz, this splitting is of the order of 1 MHz and is in agreement with the results obtained earlier by the perturbation treatments[1-3].

However, ENDOR spectroscopy has a resolution much higher than 1 MHz. The transition frequencies calculated to the third order in the power series expansion are

$$\nu_1 = \nu_p - \frac{1}{2}a + \frac{1}{2}\frac{a^2}{\nu_e + \nu_p} - \frac{1}{4}\frac{a^3}{(\nu_e + \nu_p)^2},$$

$$\nu_2 = \nu_p - \frac{1}{2}a + \frac{1}{2}\frac{a^3}{(\nu_e + \nu_p)^2}, \tag{4}$$

for the $S_z = 1/2$ branch, and

$$\nu_1' = \nu_p + \frac{1}{2}a + \frac{1}{2}\frac{a^2}{\nu_e + \nu_p} + \frac{1}{4}\frac{a^3}{(\nu_e + \nu_p)^2},$$

$$\nu_2' = \nu_p + \frac{1}{2}a - \frac{1}{2}\frac{a^3}{(\nu_e + \nu_p)^2}. \tag{5}$$

for the $S_z = -1/2$ branch. One readily sees that the splittings in the two branches are not the same, the difference being

$$\delta = \frac{3}{2}\frac{a^3}{(\nu_e + \nu_p)^2}. \tag{6}$$

For methylene proton couplings of about 100 MHz and $\nu_0 \cong 9.1$ GHz, $\delta = 20$ kHz. The accuracy of ENDOR measurements is about 10 kHz. Detailed measurements on 1-methyl uracil and thymidine available to us, although being on the border of resolution, seem to support the predictions of the theory.

It should be noted that the procedure of Pryce[4)] extended to the third order leads to the correction given by Equ. (6), except for the numerical factor 3/2.

3. *Three-proton case*

The case of three magnetically equivalent protons can be treated in the same way. The total nuclear spin can be either $I = 3/2$ or $I = 1/2$. For $I = 3/2$, the transition frequencies in the $S_z = 1/2$ branch are

$$\begin{aligned} \nu_1 &= \nu_p - \frac{1}{2}a + \frac{3}{4}\frac{a^2}{\nu_e + \nu_p} - \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}, \\ \nu_2 &= \nu_p - \frac{1}{2}a + \frac{1}{4}\frac{a^2}{\nu_e + \nu_p} + \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}, \\ \nu_3 &= \nu_p - \frac{1}{2}a - \frac{1}{4}\frac{a^2}{\nu_e + \nu_p} + \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}. \end{aligned} \tag{7}$$

For $I = 1/2$, one obtains

$$\nu = \nu_p - \frac{1}{2}a + \frac{1}{4}\frac{a^2}{\nu_e + \nu_p}. \tag{8}$$

The transition frequencies in the $S_z = -1/2$ branch are

$$\begin{aligned} \nu_1' &= \nu_p + \frac{1}{2}a + \frac{3}{4}\frac{a^2}{\nu_e + \nu_p} + \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}, \\ \nu_2' &= \nu_p + \frac{1}{2}a + \frac{1}{4}\frac{a^2}{\nu_e + \nu_p} - \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}, \\ \nu_3' &= \nu_p + \frac{1}{2}a - \frac{1}{4}\frac{a^2}{\nu_e + \nu_p} - \frac{3}{4}\frac{a^3}{(\nu_e + \nu_p)^2}, \end{aligned} \tag{9}$$

for spin $I = 3/2$, and

$$\nu' = \nu_p + \frac{1}{2} a + \frac{1}{4} \frac{a^2}{\nu_e + \nu_p}. \tag{10}$$

for spin $I = 1/2$.

From Equs. (7) and (9) one finds that the splitting $(\nu_1 - \nu_3)$ in the $S_z = 1/2$ branch differs from the splitting $(\nu_1' - \nu_3')$ in the $S_z = - 1/2$ branch by

$$\Delta = 3 \frac{a^3}{(\nu_e + \nu_p)^2}. \tag{11}$$

For typical methyl proton couplings of about 50 MHz, $\Delta < 10$ kHz and this difference could not be detected by ENDOR.

Another interesting feature of the three-proton case comes from the comparison of transitions in the $I = 3/2$ and $I = 1/2$ states. From the three generally observed lines, the middle one is obviously a closely spaced doublet, the splitting being $(3/4) \cdot a^3/(\nu_e + \nu_p)^2$. A typical splitting of about 1 kHz is small in comparison with the linewidth ($\cong$ 100 kHz) and cannot be resolved by ENDOR. If, however, the population of the $I = 3/2$ and $I = 1/2$ states is equal, i. e., the zero-field splitting between the $I = 3/2$ and $I = 1/2$ levels is small in comparison with kT, the middle line should be three times more intense than the two outer ones. The existing ENDOR measurements indicate such a possibility, although the presence of other factors influencing the intensities, such as cross relaxation2) and superposition of several ESR lines*), might obscure this effect. Careful measurement of the temperature and frequency dependence of the intensities of ENDOR methyl proton resonances in a suitable crystal offers a possibility of determining the zero-field separation between the $I = 3/2$ and $I = 1/2$, which would otherwise be very difficult to measure.

References

1) D. H. Whiffen, Mol. Phys. **10** (1966) 595;

2) S. F. J. Read and D. H. Whiffen, Mol. Phys. **12** (1967) 159;

3) P. Gloux, Mol. Phys. **21** (1971) 829;

4) M. H. L. Pryce, Proc. Phys. Soc. **A63** (1950) 25.

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*) J. N. Herak, N. Dalal and C. A. McDowell, private communication.

TOČNA RJEŠENJA ZA PRIJELAZE ENDOR MAGNETSKI EKVIVALENTNIH PROTONA

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Sadržaj

Dobivena su točna rješenja u rješavanju problema vlastitih vrijednosti spinskog hamiltonijana za nesparen elektron i dva ili tri magnetski ekvivalentna protona.

Pored cijepanja reda veličine $a^2/(\nu_e + \nu_p)$ u gornjoj i u donjoj grani spektra elektronsko-nuklearne dvostruke rezonancije (ENDOR), dobiju se i razlike reda veličine $a^3/(\nu_e + \nu_p)^2$ u cijepanjima u dvije grane.

Teorija pokazuje da se za tri ekvivalentna protona (rotirajuća metilna grupa), rezonantne linije koje pripadaju stanju $I = 1/2$ mogu opaziti u prisutnosti linija koje pripadaju stanju $I = 3/2$ samo po relativnim intenzitetima opaženih linija.