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Abstract

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HYPERFINE STRUCTURE OF E.P.R. SPECTRA IN A ONE-ELECTRON SYSTEM WITH TWO POTENTIAL WELLS

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Let us consider an electron in a system of two symmetric potential wells (Fig. 1), whose Hamiltonian has the form

$$H_0 = \hat{H}_0 + \hat{H}'; \tag{1}$$

$$\hat{H}_0 = \hat{E}_0 - \beta_0 \hat{S}_z H_z - \beta \left[\sum_{l=1}^{n} I_z^l H_z + \sum_{l'=1}^{n'} I_z^{l'} H_z \right], \tag{2}$$

$$\hat{H}' = \hat{V} + \hat{R} = \hat{V} - \frac{16\pi\beta_0\beta}{3c} \left[\sum_{l=1}^{n} \delta(\mathbf{r} - \mathbf{r}_l)\, \hat{S}\hat{I}_z^l + \sum_{l'=1}^{n'} \delta(\mathbf{r} - \mathbf{r}_{l'})\, S I_z^{l'} \right]. \tag{3}$$

The first term in (2) is the operator of the orbital motion of the electron in a separate well; the second is the interaction of the magnetic moment of the electron $\beta_0\hat{S}$ with the external constant magnetic field H_z, and the third is the energy of the nuclear magnetic moments $\beta_l \hat{I}^l$ in the same field; the index l denotes nuclei located in the right potential well, and l' those in the left. The first term in the perturbation operator (3) represents the additional small energy introduced by the presence of the neighboring well, which, for an assumed large barrier, may be regarded as a perturbation. The remaining part of the perturbation $\hat{R}$ is associated with the hyperfine interaction of the electron spin with the nuclei. It is assumed that we are dealing with purely spin magnetism and that only the Fermi contact term remains in the hyperfine interaction.

As the initial representation, choose the eigenvectors of the operators $\hat{E}_0, \hat{S}_z, \hat{I}_z^l, \hat{I}_z^{l'}$, and denote them by $\psi(k, s, i_l, i_{l'})$, where s, i_l, and $i_{l'}$ are the eigenvalues of the operators $\hat{S}_z, \hat{I}_z^l, \hat{I}_z^{l'}$, while k takes only the two values 1 and 2, corresponding to the two possible coordinate functions

Fig. 1

Figure 1: Fig. 1

$$\psi_1(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\psi(\mathbf{r}) + \psi(-\mathbf{r})\right], \qquad \psi_2(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\psi(\mathbf{r}) - \psi(-\mathbf{r})\right]. \tag{4}$$

Here $\hat{E}_0\psi(\pm\mathbf{r}) = E_0\psi(\pm\mathbf{r})$.

The Hamiltonian of the unperturbed problem is diagonal in this representation, and each of its terms is doubly degenerate with respect to the orbital quantum number k:

$$\langle k, s, i_l, i_{l'}|\hat{H}_0|k', s', i'_l, i'_{l'}\rangle : \left\{E_0 - \beta_0 H s - \beta H\left[\sum_{l'=1}^{n} i_l + \sum_{l'=1}^{n'} i_{l'}\right]\right\} \times$$

$$\times \delta_{kk'}\delta_{ss'}\delta_{i_l i'_l}\delta_{i_{l'} i'_{l'}}. \tag{5}$$

The matrix of the operator $\hat{V}$ is, of course, diagonal in all spin variables. Moreover, owing to the choice of the coordinate wave functions in the form (4), it is also diagonal in the variables k, so that

$$\langle k, s, i_l, i_{l'}|\hat{V}|k', s', i'_l, i'_{l'}\rangle = (-1)^k t\delta_{kk'}\delta_{ss'}\delta_{i_{li}l'}\delta_{i_{l'}i'_{l'}}, \tag{6}$$

where the quantity b can, under certain conditions, be calculated quasiclassically [(2)]. Usually the interaction with the external field is much stronger than the hyperfine coupling (Paschen–Back effect), and therefore the products $\hat{S}\hat{I}^l$ in the operator $\hat{R}$ may be replaced by $\hat{S}_z\hat{I}^l_z$. As a result the operator $\hat{R}$ becomes diagonal in the variables s, i, and i', and its nonzero elements, found by direct calculation with the aid of (3) and (4), are equal to:

Fig. 1

$$\langle k, s, i_l, i_{l'}|\hat{R}|k, s, i_l, i_{l'}\rangle = \sum_{l=1}^{n}\delta_{lsi}l + \sum_{l'=1}^{n'}\delta_{l's i_{l'}}; \tag{7a}$$

$$\langle k, s, i_l, i_{l'}|\hat{R}|k', s, i_l, i_{l'}\rangle = \sum_{l=1}^{n}\delta_{lsi}l - \sum_{l'=1}^{n'}\delta_{l's i_{l'}} = t(s, i_l, i_{l'}); \tag{7b}$$

the hyperfine-structure constants

$$\delta_l = -\frac{16\pi\beta_0\beta}{3c}\,\frac{1}{2}|\psi(\mathbf{r}_l)|^2 > 0; \qquad \delta_{l'} = -\frac{16\pi\beta_0\beta}{3c}\,\frac{1}{2}|\psi(\mathbf{r}_{l'})|^2 \tag{8}$$

correspond to an electron distributed uniformly over both nuclei.

The energy spectrum of the system is found by solving the secular problem. Since H' is diagonal in all spin variables, it essentially reduces to finding the correct coordinate wave functions of the zeroth approximation $\psi^0(r, s, i_l, i_{l'})$ and the corresponding corrections to the energy $\Delta E(r, s, i_l, i_{l'})$. The index r, as well as k, takes only two values, 1 and 2; it is quantized by the value of the total energy H.

In view of (6) and (7), the secular equation has the form

$$\begin{vmatrix} -b + \sum_{l=1}^{n} \delta_{lsi} l + \sum_{l'}^{n} \delta_{l'} s i_{l'} & t(s, i_l, i_{l'}) \\ t(s, i_l, i_{l'}) & b + \sum_{l=1}^{n} \delta_{lsi} l + \sum_{l'=1}^{n'} \delta_{l'} s i_{l'} \end{vmatrix} = 0. \tag{9}$$

The corrections to the energy are equal to [(1)]:

$$\Delta E(1, s, i_l, i_{l'}) = \sum_{l=1}^{n} \delta_{lsi} l + \sum_{l'=1}^{n'} \delta_{l'} s i_{l'} - \sqrt{b^2 + t^2}; \tag{10a}$$

$$\Delta E(2, s, i_l, i_{l'}) = \sum_{l=1}^{n} \delta_{lsi} l + \sum_{l'=1}^{n'} \delta_{l'} s i_l + \sqrt{b^2 + t^2}, \tag{10b}$$

and the elements of the matrix C_k^r, which carries out the canonical transformation from the initial representation to the desired one, are equal to:

$$C_1^1 = \sqrt{\frac{t}{2|t|}\left[1 + \frac{b}{\sqrt{b^2 + t^2}}\right]}; \qquad C_2^1 = -\sqrt{\frac{|t|}{2t}\left[1 - \frac{b}{\sqrt{b^2 + t^2}}\right]}; \tag{11a}$$

$$C_1^2 = \sqrt{\frac{t}{2|t|}\left[1 - \frac{b}{\sqrt{b^2 + t^2}}\right]}; \qquad C_2^2 = \sqrt{-\frac{|t|}{2t}\left[1 + \frac{b}{\sqrt{b^2 + t^2}}\right]}. \tag{11b}$$

The notation is chosen so that for $b \gg t > 0$ the new representation coincides with the old one:

$$\psi^0(r, s, i_l, i_{l'}) = \sum_{k=1}^{2} C_k^r \psi(k, s, i_l, i_{l'}) = C_1^r \psi(1, s, i_l, i_{l'}) + C_2^r \psi(2, s, i_l, i_{l'}). \tag{12}$$

It follows from (12), (11), and (4) that for $b \gg t$ the stationary wave function corresponds to an electron uniformly distributed over both nuclei, while for $b \ll t$ it corresponds to one localized only at one of them. For $t = 0$

$$\left(\sum_{l}^{n} \delta_l i_l = \sum_{l'}^{n'} \delta_{l'} i_{l'} \right)$$

the electron is always uniformly distributed over both nuclei, irrespective of the magnitude of b.

We are interested in the electronic transitions that arise in the system under consideration under the action of an alternating magnetic field. The time-dependent part of the Hamiltonian is in this case $\beta_0 H_x(t)\hat{S}_x$, and, in accordance with the correspondence principle, the intensities of the excited spectral lines are determined by the relation

$$I(r, s, i_l, i_{l'} \to r', s', i'_l, i'_{l'}) = \gamma \left| \langle r, s, i_l, i_{l'} | \hat{S}_x | r', s', i'_l, i'_{l'} \rangle \right|^2 =$$

$$= \gamma \left| \langle r | r' \rangle_s \right|^2 \delta^0_{ss'\pm 1} \delta^0_{i_l i'_l} \delta^0_{i_{l'} i'_{l'}}, \tag{13}$$

where, by virtue of (12) and the orthogonality of $\psi(k, s, i_l, i_{l'})$,

$$\langle r | r' \rangle_s = 2\psi^{0*}(r, s, i_l, i_{l'}) \hat{S}_x \psi^0(r', s \pm 1, i_l, i_{l'}) =$$

$$= C_1^r(s) C_1^{r'}(s \pm 1) + C_2^r(s) C_2^{r'}(s \pm 1). \tag{14}$$

According to (11), (13), and (14), the allowed transitions obey the selection rules $\Delta i_l = \Delta i_{l'} = 0$, $\Delta s = \pm 1$, and split into two groups with intensities

$$I_{i_l, i_{l'}}(r|r) = \gamma \frac{b^2}{b^2 + t^2}, \tag{15a}$$

$$I_{i_l, i_{l'}}(r|r') = \gamma \left(1 - \frac{b^2}{b^2 + t^2} \right). \tag{15b}$$

It is remarkable that even within each group the transition intensities are not the same for all lines, but depend, through $t(1/2, i_l, i_{l'})$, on the orientation of the nuclear spins of the molecule undergoing the given transition. Nevertheless, the total intensity corresponding to the given t is constant:

$$I_{i_l i_{l'}}(r|r) + I_{i_l i_{l'}}(r|r') = \gamma = \text{const}.$$

It goes without saying that formulas (15) give only the integral intensity of the hyperfine components of the spectrum, which under monochromatic excitation have a resonance character with a width depending on relaxation processes.

The line frequencies corresponding to the two allowed groups of transitions are, obviously, equal to

$$h\nu_{i_l i_{l'}}(1|1) = \beta_0 H_z + \sum_{l=1}^{n} \delta_l i_l + \sum_{l'=1}^{n'} \delta_{l'} i_{l'} = h\nu_{i_l i_{l'}}(2|2); \tag{16a}$$

$$h\nu_{i_l i_{l'}}(1|2) = \beta_0 H_z + \sum_{l=1}^{n} \delta_l i_l + \sum_{l'=1}^{n'} \delta_{l'} i_{l'} - 2\sqrt{b^2 + t^2}; \tag{16b}$$

$$h\nu_{i_l i_{l'}}(2|1) = \beta_0 H_z + \sum_{l=1}^{n} \delta_l i_l + \sum_{l'=1}^{n'} \delta_{l'} i_{l'} + 2\sqrt{b^2 + t^2}.$$

To illustrate the results, Fig. 2 shows spectra of a system in which in each nucleus there is only one nuclear spin i and i' of magnitude $1/2$, in three different cases: $b \gg t$, $b = t$, $b \ll t$. The outer lines in these spectra refer to the allowed transitions of the second group (formulas (15b) and (16b)), and the remaining ones to the first group (formulas (15a) and (16a)), with two transitions, coinciding in ···

frequency. As b decreases, these latter transitions become forbidden and the central line dies out, whereas the outer lines, on the contrary, increase in intensity and tend toward the two middle lines, merging with them as $b \to 0$. The lines that are variable in intensity (at the center and at the edges) are associated with transitions in which $i = -i'$, which corresponds to wells differing in the orientations of the nuclear spin. The middle lines, which remain unchanged for any ratio between b and t, correspond to transitions with $i = i'$, which occur in molecules with complete spatial symmetry.

The spectrum in the case $b \gg t$ is ordinary in the sense that it can be interpreted as the hyperfine structure from an electron uniformly distributed over both wells, independently of the orientation of the nuclear spins in them. The opposite limiting case, in external appearance, corresponds to an electron localized in only one of the wells (as a result of which the splitting is twice as large as in the preceding case); however, in reality, both the outer components of the spectrum ($i = -i'$), for which this statement is true, and the middle lines ($i = i'$), which in any case correspond to a uniformly distributed electron, contribute to the observed picture.

Fig. 2

It should, of course, be borne in mind that one or another type of electron distribution in the molecule is preserved for a time interval of the order of

Fig. 2

Figure 2: Fig. 2

$$\frac{T_1}{n+n'},$$

where T_1 is the time of longitudinal relaxation of the nuclei. After this interval has elapsed, $t(^{1/2}, i_1, i_1')$ changes, and the electron density is redistributed accordingly. The hyperfine structure of the spectrum in the intermediate case ($b \sim t$) is very complex. On its basis, the magnitude b can be calculated from (15) or (16). Unfortunately, however, the change from the spectrum at $b \gg t$ to the spectrum at $b \ll t$ occurs in so narrow an energy interval that it is very difficult to detect experimentally. Therefore, so far only the limiting cases have been studied in detail [2].

It is easy to see that, in the most general case as well, the assertion "the electron is located in two wells" means only that $b \gg t$. In the opposite case ($b \ll t$), the perturbation of the system breaks the symmetry of the wells and localizes the electron in that one of them in which its energy proves to be lower. In the case of an unperturbed molecule ($b \gg t$), the electron is "uniformly distributed"between the wells and undergoes periodic transitions between them with frequency $2b/\hbar$. This process differs from the radioactive decay of a particle overcoming the barrier of a nucleus in that the electron cannot leave the limits of the system, and its motion, for this reason, has a periodic character.

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