ON THE THEORY OF THE ANISOTROPY OF HYPERFINE SPLITTING IN THE E.P.R. SPECTRA OF FREE RADICALS

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Abstract

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ON THE THEORY OF THE ANISOTROPY OF HYPERFINE SPLITTING IN THE E.P.R. SPECTRA OF FREE RADICALS

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The hyperfine splitting observed in the e.p.r. spectra of free radicals is usually due to the Fermi interaction of the spin of the unpaired electron with the spins of the nuclei of the radical and is therefore isotropic. However, in a number of cases (for example, (1−5)) e.p.r. spectra exhibit a considerable anisotropy of the hyperfine splitting. McConnell and Strathdee (6) estimated the anisotropy tensor $A_{\alpha\beta}$ of π-electron radicals, but in their work certain assumptions were made which, while correctly explaining the order of magnitude of the anisotropic interaction, lead to underestimated values of the isotropic splitting constant. We further note that in the literature (7,8) the Fermi interaction is often regarded as having no analogue in nonrelativistic theory; but, as is known (9), this is not so.

The hyperfine interaction in e.p.r. spectra is described by the following terms of the spin Hamiltonian $\mathscr{H}_S$:

$$\mathscr{H}_S = \frac{g g_N}{c} \beta \beta_N \left(A^0 \mathbf{SI} + A_{\alpha\beta} S_\alpha I_\beta \right), \tag{1}$$

where A^0 is the isotropic part of the hyperfine interaction; the remaining designations are conventional. This interaction may be interpreted as the interaction of the magnetic moment of the nucleus with the magnetic field created by the spins of the electrons. The magnitude of this field is determined by the value of the spin current $\mathbf{j}_S$.

In order to determine $\mathbf{j}_S$ in the case of a many-electron system of interest to us, let us note that the mean value of the Hamiltonian

$$\hat{\mathscr{H}} = U(x_1, \dots, x_n) + \sum_{i=1}^{n} \left\{ \frac{1}{2\mu_i} \left(\hat{\mathbf{p}}_i - \frac{e_i}{c} \mathbf{A}_i \right)^2 + g_i \beta_i \mathbf{H}_i \mathbf{S}_i \right\} \tag{2}$$

(the potential U includes all interactions independent of the vector potential $\mathbf{A}$; $\hat{\mathbf{p}}_i$ is the generalized momentum, μ_i the electron mass), by virtue of the identity of the electrons, can be represented in the form

$$\overline{\mathcal{H}} = U + \int \Psi^* \left\{ \frac{n}{2\mu} \left(\hat{\mathbf{p}} - \frac{e}{c}\mathbf{A} \right)^2 - g\beta \mathbf{H} S \right\} \Psi \, dv_n, \tag{3}$$

where $\hat{\mathbf{p}}$ refers to some one electron; $\mathbf{A}$ and $\mathbf{H}$ are taken at the point where this electron is located; $\mathbf{S}$ is the total spin of the system; U is a constant independent of $\mathbf{A}$. Further reasoning is analogous to the derivation of the current-density formula for a single particle (9) and leads to the result:

$$\mathbf{j}_S = g \cdot \beta \text{ rot } \vec{\rho}_S, \tag{4}$$

where $\vec{\rho}_S$ is the first-order spin-density matrix, defined by the expression $\vec{\rho}_S = \int \Psi \mathbf{S} \Psi \, dv_{n-1}$; $\int dv_{n-1}$ denotes integration over the pro-

spatial coordinates of all electrons except one and summation over all spin coordinates. In deriving formula (4) we assumed that the state of the system under consideration is a Kramers doublet (as a consequence of which in (4) the function Ψ may be regarded as real).

The magnetic field $\mathbf{H}_S$, produced by the current $\mathbf{j}_S$, is, by the Biot–Savart law,

$$\mathbf{H}_S = \frac{g\beta}{c} \int \left[\nabla \frac{1}{r} \text{ rot } \rho_S \right] dv, \tag{5}$$

where r is the distance from the magnetic nucleus of interest to the electron. Separating out a small sphere ε near the nucleus and transforming the integral entering (5) analogously to what was done in Ref. (^{9}), we find:

$$H_{S\alpha} = \frac{g\beta}{c} \left(\frac{8\pi}{3} \rho_S(0) + A_\alpha \right), \tag{6}$$

where

$$A_\alpha = \lim_{\varepsilon \to 0} \int_{V-\varepsilon} \rho_{S\beta} \frac{3 r_\alpha r_\beta - r^2 \delta_{\alpha\beta}}{r^5} \, dv. \tag{7}$$

The energy of the magnetic moment of the nucleus in the magnetic field produced by the electron spins is

$$\mathcal{H}_S = -g_N \beta_N H_{S\alpha} I_\alpha. \tag{8}$$

Assuming that the spin-density matrix $\rho_{S\alpha}$ can be represented as the product of the projection of the total spin S_α by some ρ independent of α: $\rho_{S\alpha} = \rho S_\alpha$, and comparing, under this condition, formulas (1) and (8), (6), we find

$$A^0 = \frac{8\pi}{3}\rho(0); \tag{9}$$

$$A_{\alpha\beta} = \lim_{\varepsilon\to 0}\int_{V-\varepsilon}\rho\,\frac{3r_\alpha r_\beta - r^2\delta_{\alpha\beta}}{r^5}\,dv. \tag{10}$$

Let us note that formulas (6)–(8) are valid for an arbitrary number of interacting electrons; expressions (9)–(10) are obtained with the aid of (6)–(8) and the assumption made above concerning the form of ρ_S, which corresponds to a one-electron approximation. Thus, the formulas obtained make it possible to calculate the isotropic and anisotropic parts of the hyperfine interaction.

Let us now consider the frequently occurring case in which the density matrix ρ (i.e., the spin-density distribution of the unpaired electron) has a symmetry axis of the second order, and the nucleus whose magnetic moment interacts with the electron lies on this axis. Suppose further that there is a plane passing through the same axis with respect to which ρ is also symmetric (symmetry C_2). Then it is obvious that in a coordinate system whose Z axis is directed along the symmetry axis, whose Y axis lies in the plane of symmetry and is perpendicular to the symmetry axis, and for which the positive direction of the X axis is chosen arbitrarily, the tensor $A_{\alpha\beta}$ is diagonal (it is seen directly from formula (10) that the chosen coordinate system coincides with the principal axes of this tensor). Now, with the aid of (10), it is not difficult to obtain the following expressions for the principal values of the anisotropy tensor of the hyperfine interaction:

$$A_{zz} = 2t_0(\rho); \qquad A_{yy} = -\left(t_0(\rho) + {}^1\!/_2 t_2(\rho)\right); \qquad A_{xx} = -\left(t_0(\rho) - {}^1\!/_2 t_2(\rho)\right), \tag{11}$$

where

$$t_0(\rho) = \int \rho\,\frac{1}{r^3}Y_2^{(0)}(\vartheta,\varphi)\,dv; \qquad t_2(\rho) = \int \rho\,\frac{1}{r^3}Y_2^{(-2)}(\vartheta,\varphi)\,dv,$$

and $Y_l^m(\vartheta,\varphi)$ is a spherical function (we have chosen a spherical coordinate system with its origin at the nucleus of interest).

As an example, let us consider the anisotropy of the hyperfine splitting on α-protons of π-electron radicals. Since the dipole-dipole interaction rapidly decreases with distance, one may restrict oneself to taking account of the electron density only in the vicinity of the proton and consider a simple three-electron model of a C–H fragment (10). In this model the wave function Ψ is chosen in the form $\Psi = \Psi_1 + \lambda\Psi_2$, where Ψ_1 describes the state in which the unpaired electron is on the π-orbital of the C atom, while Ψ_2 corresponds to the state in which the π-electron of the C atom is paired with one of the electrons of the σ-bond C–H; here $\lambda = -H_{21}/\Delta E_{21}$, $H_{21} = \int \Psi_2 H \Psi_1\,d\tau$, $\Delta E_{21} = H_{22} - H_{11}$.

In this model the spin density, accurate to λ (as numerical calculation shows, $\lambda = 0.1 \div 0.01$), is equal to

$$\rho_S = \rho_S(\pi\pi) + \rho_S(\sigma\sigma^*), \qquad \rho_S(\pi\pi) = \frac{1}{2}\pi^2, \qquad \rho_S(\sigma\sigma^*) = \lambda\sqrt{\frac{2}{3}}\,\sigma\sigma^*, \tag{12}$$

where π is the one-electron wave function of the π-electron; σ and σ^* are the wave functions of the ground and excited states of the C—H bond.

For estimation we put $\sigma = \frac{1}{N_\sigma}\{\chi + (1+q)h\}$, $\sigma^* = \frac{1}{N_{\sigma^*}}\{\chi - (1+q^*)h\}$, where χ is a hybrid sp^2-orbital of carbon; h is the hydrogen $1s$ orbital; π is the Slater orbital of carbon φ_{2px}; N_σ and N_{σ^*} are normalization factors. The coefficient q determines the degree of polarity of the C—H bond; q^* can be found from the condition of orthogonality of the orbitals σ and σ^*. For the spin density ρ_S of the form (12), according to (11) we obtain $t_2(\rho) = t_2(\pi\pi)$ by virtue of the cylindrical symmetry of the σ-bond; moreover,

$$t_0(\rho) = t_0(\pi\pi) + t_0(\sigma\sigma^*), \tag{13}$$

where

$$t_0(\sigma\sigma^*) = \lambda\sqrt{\frac{2}{3}}\,\frac{1}{N_\sigma N_{\sigma^*}}\left\{t_0(\chi\chi) + q\,\frac{2+q}{1+s_0+q}\,t_0(\chi h)\right\},$$

$$t_0(\chi\chi) = \frac{1}{3}\{t_0(\varphi_{2S}^2) + 2t_0(\varphi_{2pz}^2) + 2\sqrt{2}\,t_0(\varphi_{2pz}\varphi_{2S})\}, \tag{14}$$

$$t_0(h\chi) = \frac{1}{\sqrt{3}}\{t_0(h\varphi_{2S}) + \sqrt{2}\,t_0(h\varphi_{2pz})\}, \qquad s_0 = \int \chi h\,dv.$$

The quantities $t_0(\varphi_{2px}^2)$, $t_0(\varphi_{2px}^2)$, $t_0(\varphi_{2pz}^2)$, $t_0(\varphi_{2S}^2)$, and $t_0(\varphi_{2S}\varphi_{2pz})$ can be calculated from the formulas of work (6). We carried out the calculation of the integrals $t_0(h\varphi_{2S})$ and $t_0(h\varphi_{2pz})$, which contain exchange densities, in two-center coordinates r_c and r_h, with subsequent passage to the limit (see formulas (7), (11)). Putting $R_{\text{CH}} = 1.088$ Å, $z_C = 3.18$, $z_H = 1$, where R_{CH} is the distance between the C and H atoms, and z_C and z_H are the effective charges of the C and H atoms respectively, we obtain:

$$t_0(\sigma\sigma^*) = \lambda(0.041 - q\cdot 0.28), \qquad t_0(\pi\pi) = 0.040, \qquad t_2(\pi\pi) = 0.064; \tag{15}$$

the quantities t are expressed in atomic units.

The polarity q can be estimated by using the wave function of the ground state of the radical CH_3 $^{(11)}$, which gives $q = -0.17$. The value $-q = 0.1 \div 0.2$ is also consistent with the calculation of the dipole moment of the C—H bond in the ethylene molecule $^{(12)}$. Thus, allowance for the polarity of the C—H bond increases the value $t_0(\sigma\sigma^*)$ by approximately a factor of two. Nevertheless, for reasonable values of the parameter $\lambda = 0.1 \div 0.01$ we obtain that $t_0(\sigma\sigma^*)$ is substantially smaller than $t_0(\pi\pi)$. In other words, the anisotropy of the hyperfine splitting for π-electron radicals is determined primarily

of the total π-electron distribution; the contribution of the σ-electron distribution, even allowing for the polarity of the C—H bond, is small.

Let us note that the conclusion we have obtained concerning the smallness of the contribution to the value of $A_{\alpha\beta}$ from the electrons of the σ bond is not of a general character; this conclusion is valid only for radicals whose electronic structure corresponds to the model considered by us.

In estimating the π- and σ-electron contributions to the tensor of the anisotropic hyperfine interaction, McConnell and Strathdee (^{6}), proceeding from a somewhat different model, arrived at the conclusion that the value $t_0(\sigma\sigma^*)$, caused by the σ-electron spin density, may be comparable with the contribution of the π-electron distribution $t_0(\pi\pi)$; moreover, they did not take into account the possible polarity of the C—H bond, which increases $t_0(\sigma\sigma^*)$. The quantity $t_0(\sigma\sigma^*)$ is proportional to the weight of the σ-electron spin density; putting $\lambda = 0.1 \div 0.01$, according to the results of work (^{6}), we find that $t_0(\sigma\sigma^*)$ and $t_0(\pi\pi)$ are of the same order, but the values of $A_{\alpha\beta}$ calculated under this condition differ substantially from the experimental ones. Therefore, in comparing the calculated values of $A_{\alpha\beta}$ with the experimental data, McConnell and Strathdee (^{6}) assumed that $\lambda \simeq 0$, whereas to explain the magnitude of the isotropic hyperfine splitting it is necessary to take $\lambda \simeq 0.03$.

Calculating from formulas (11), (15) the components of the tensor of the anisotropic hyperfine interaction due to the contribution of the π-electrons, we find:

$$gg_N \frac{\beta\beta_N}{c} A_{zz} = 43 \text{ Mc/s}; \qquad gg_N \frac{\beta\beta_N}{c} A_{xx} = -5 \text{ Mc/s};$$

$$gg_N \frac{\beta\beta_N}{c} A_{yy} = -38 \text{ Mc/s}.$$

Experimentally, for a series of π-electron radicals, the following has been obtained ($^{1-6}$):

$$gg_N \frac{\beta\beta_N}{c} A_{zz} = 31 \div 26 \text{ Mc/s}; \qquad gg_N \frac{\beta\beta_N}{c} A_{xx} = -1 \div +7 \text{ Mc/s};$$

$$gg_N\frac{\beta\beta_N}{c}A_{yy}=-(37\div 28)\ \text{Mc/s}.$$

As is seen, the agreement between the calculated and experimental values of the anisotropy of the hyperfine interaction is quite satisfactory.

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