VARIATIONAL ANALYSIS OF ISOTROPIC E.P.R. SPECTRA IN FOURIER SPACE

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VARIATIONAL ANALYSIS OF ISOTROPIC E.P.R. SPECTRA IN FOURIER SPACE

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The analysis of poorly resolved e.p.r. spectra is a topical but difficult problem. To date, a number of works have been carried out in this field (see the review (^{1})); however, the problem of analyzing complex spectra in general remains unresolved. Here we describe a new procedure for finding the parameters of an isotropic symmetric spectrum, based on comparison of the correlation function of the experimental spectrum with a theoretically calculated one.

It was shown earlier (^{2}) that the correlation function $F(t)$ and the isotropic spectrum $A(z)$ are related by

$$F(t) = \int_{-\infty}^{\infty} A(z) \exp(itz)\, dz = C\varphi_\Phi(t) \prod_{\substack{k=1\\ s=1}}^{H,N} \cos\left({}^1/_2\, a_k t\right) \left(1 + 2\cos(b_s t)\right);$$

here z is the current value of the magnetic field; t is a parameter having the meaning of time; H and N are the numbers of isotropic h.f.s. constants with values a_k and b_s for $I = {}^1/_2$ and $I = 1$, respectively; $\varphi_\Phi(t)$ is the correlation function of an individual line, which we described in the form

$$\varphi_\Phi(t) = t \exp\left(-\frac{\sqrt{3}}{2}\Delta H_{\mathrm{L}}|t| - \frac{1}{8}\Delta H_{\mathrm{G}}^2 t^2\right).$$

Thus we assumed in advance that the e.p.r. spectrum is recorded in the form of the first derivative (the factor t) and that the individual line is described by a composition of Lorentzian and Gaussian distributions (ΔH_{L} and ΔH_{G} are the line widths at the points of maximum slope).

According to Parseval' s theorem (^{3}),

$$\int_{-\infty}^{\infty} \left(A_{\mathrm{T}}(z) - A_{\mathrm{e}}(z)\right)^2\, dz = \int_{-\infty}^{\infty} \left(F_{\mathrm{T}}(t) - F_{\mathrm{e}}(t)\right)^2\, dt = \min,$$

therefore the extraction of constants from the spectrum can be carried out either by comparing the theoretical spectrum $A_{\mathrm{T}}(z)$ with the experimental one $A_{\mathrm{e}}(z)$ in the mean-square sense, or by comparing, in the same sense, their correlation functions ([1,4]). The use of $F(t)$ instead of $A(z)$ makes it possible to choose the best trial h.f.s. constants, since the roots of the Fourier integral of the spectrum $A(z)$ are connected only with the h.f.s. constants ([2]) and do not depend on the degree of resolution of the spectrum. In addition, the function $F(t)$ permits a fairly simple analytical expression for a spectrum of arbitrary complexity, and the correlation function $F(t)$ in the region of small t depends only slightly on high-frequency noise in the experimental spectrum ([5]), which is also significant in determining the parameters of the spectrum.

For the analysis of real symmetric isotropic e.p.r. spectra within the framework of the adopted model, three programs were compiled:

1. Calculation of the Fourier integral $F_{\mathrm{e}}(t)$ from the initial spectrum was carried out according to Filon' s formula ([6]). The values of the Fourier integral and preliminary values of the h.f.s. constants, calculated according to formulas ([2]), were printed out.

2. The trial values of the constants were varied until the best agreement (in the least-squares sense) was obtained between the theoretical $F_{\mathrm{r}}(t)$ and experimental $F_{\mathrm{e}}(t)$ correlation functions. To find the minimum, the Hooke and Jeeves procedure ([7]) was used; in this procedure the search process is substantially accelerated if the search direction is chosen correctly. In carrying out the analysis of real spectra it was found that, if the number of trial constants exceeds the number of constants in the experimental spectrum, the superfluous constants are close to zero. Conversely, if the number of trial constants is smaller than necessary, the parameters ΔH_{L} and ΔH_{G} increase substantially, and the spectrum constructed from the constants found proves to be blurred.

Fig. 1. *a*—experimental spectrum of 2,6-di-tert-butyl-4-(4′-tert-butyl)-phenoxy radical; *b*—theoretical spectrum with parameters calculated by the method described in the text.

3. To check the constants found, a computer program was written for calculating the theoretical spectra $A_{\mathrm{t}}(z)$ from specified parameters, with output of the line-shape function to a plot. The effectiveness of the programs written was tested on a number of experimental and theoretical spectra. Below is an example of the analysis of the spectrum of a radical with a concentration of $\sim 10^{17}$ particles/liter in diethyl ether at room temperature. Recording of the curve was carried out with the maximum reduction of noise distorting the spectrum. The center of the spectrum was not determined in advance. The origin of coordinates was chosen at the extreme left end of the spectrum, where $A'(z) = 0$. From the experimental curve 253 points were taken. Calculation of the Fourier integral took about 5 min. With the second program, ΔH_{L}, ΔH_{G}, a_1, a_2, a_3, a_4, a_5, a_6, and the po-

sition of the center of the spectrum were calculated. Each iteration lasted about 40 sec. The duration of the entire calculation was approximately 40 min (M-20 computer).

The results of the spectrum analysis are reproduced in Fig. 1. Satisfactory agreement of the theoretical spectra with the experimental one is seen. The calculation gave the following values of the constants: $\Delta H_{\mathrm{L}} = 0.048$ oersted, $\Delta H_{\mathrm{G}} = 0.37$ oersted, $a_1 = 1.58$ oersted, $a_2 = 1.60$ oersted, $a_3 = 1.66$ oersted, $a_4 = 1.76$ oersted, $a_5 = 0.64$ oersted, $a_6 = 0.66$ oersted. Calculation according to Hückel (^{8}) indicates that a_5 and a_6 refer to protons in positions $3'$ and $5'$, while the remaining constants refer to protons 3, 5, $2'$, $6'$. The considerable value of ΔH_{G} indicates the presence of spin density in the tri-tert-butyl substituents.

Thus, the method used makes it possible to analyze isotropic EPR spectra satisfactorily in quite an acceptable time. Apparently, a small deviation from isotropy of the spectrum will lead to only a small difference between the constants found and the true ones.

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