

## Semiclassical Theory of the Effects of Internal Motions on the Linewidths in Electron Spin Resonance Spectra\*

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A number of classical dynamical models are developed for describing the effects of internal rotational motions and solvent-complex formation on the ESR hyperfine linewidths of free radicals in solution. These dynamical processes can lead to linewidth effects because they cause time-dependent modulations of the isotropic hyperfine interactions of the different magnetic nuclei. An alternating linewidth effect, which has been observed in a number of recent studies, is predicted to result when there is an out-of-phase correlation between the hyperfine splittings  $a_i(t)$  of equivalent nuclei. By equivalent nuclei here are meant those for which the time-average splittings  $\langle a_i(t) \rangle_{Av}$  are equal, and an out-of-phase correlation is one in which an increase in the instantaneous splitting from Nucleus  $i$ ,  $a_i(t)$ , is correlated with a decrease in the splitting  $a_j(t)$  from nucleus  $j$ . This out-of-phase correlation can result from a coupling of the mechanical motions of different rotating groups and also from the effects that changes in orientations of uncorrelated rotors may have on redistributing electron spin density in the molecule. Continuous motion cases are treated by Brownian-motion theory using coupled and uncoupled internal rotors and torsional oscillators. Random jump models between discrete states are also considered. It is shown that all these models can give rise to an alternating linewidth effect provided that certain definite relationships of the proper type exist for the coupling of the motions or the variations of the spin densities. For many of these models the correlation  $a_1(t) = a_2(t)$  for all  $t$ , or complete equivalence of both nuclei, may also result when different relationships exist. The correlation of the splittings of more than two groups of completely equivalent nuclei will, in general, lead to more complex linewidth effects.

### I. INTRODUCTION

IN the last several years, a number of investigations of the electron spin resonance of free radicals have yielded spectra with anomalous linewidth variations.<sup>1-8</sup> Some of these linewidth effects have been attributed to modulations of the isotropic hyperfine splittings, a mechanism that had not been considered in the earlier theories of linewidth and saturation,<sup>9-11</sup> and their complete understanding required a reformulation of the theory of linewidths.<sup>6,12</sup> In the most striking examples, every other line in the spectrum is anomalously broadened; this is called the alternating linewidth phenom-

non. It was first observed in the highly hindered dihydroxydurene (1,4-dihydroxy-2,3,5,6-tetramethylbenzene) cation<sup>1</sup> and the dinitrodurene anion<sup>2,5</sup> radicals, but in the former the effect was detected among the lines from the methyl-group proton splittings and in the latter among the nitrogen lines. Further studies showed alternating linewidths in the spectrum of the naphthazarin (1,4,5,8-tetrahydroxynaphthalene) cation,<sup>3,13</sup> a number of other nitrobenzene anions,<sup>5,6</sup> and the pyracene anion.<sup>7</sup> The alternating linewidths in the spectra of the dihydroxydurene and naphthazarin cations arise from motions of the hydroxyl protons, those in the nitro compounds from rotational motions of the nitro groups or dynamical interactions of these groups with solvent molecules,<sup>14</sup> while in the pyracene anion the alternations in width are caused by the jumping of an alkali-metal cation between two positions in the radical. Thus a number of different dynamical phenomena can produce fluctuations in the hyperfine splittings.

Some of the explanations of the alternating linewidth phenomena attributed the effect to rapid jumps or reorientations of substituents or solvent species between a small number of different equilibrium positions,<sup>1,3,8,12,13</sup> but the revised theory of linewidths<sup>6,12</sup> indicates that considerably more general types of motions can produce the phenomena.<sup>2</sup> This theory also shows that the type of linewidth variation resulting from modulations of the isotropic splittings depends upon the nature of the correlations in the fluctua-

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<sup>1</sup> J. R. Bolton and A. Carrington, *Mol. Phys.* **5**, 161 (1962).

<sup>2</sup> J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962); J. H. Freed, I. Bernal, and G. K. Fraenkel, *Bull. Am. Phys. Soc.* **7**, 42 (1962).

<sup>3</sup> J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.* **6**, 169 (1963).

<sup>4</sup> J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1881 (1962).

<sup>5</sup> J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **41**, 699 (1964).

<sup>6</sup> J. H. Freed, thesis, Columbia University, New York, 1962.

<sup>7</sup> E. de Boer and E. L. Mackor, *Proc. Chem. Soc.* **1963**, 23.

<sup>8</sup> J. E. Harriman and A. H. Maki, *J. Chem. Phys.* **39**, 778 (1963).

<sup>9</sup> D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).

<sup>10</sup> M. J. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).

<sup>11</sup> J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961).

<sup>12</sup> J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963). References to this work are designated by I.

<sup>13</sup> A. Carrington, *Mol. Phys.* **5**, 425 (1962).

<sup>14</sup> J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962).

tions of the hyperfine interactions of the different magnetic nuclei present in the free radical. Thus in some circumstances instead of an alternating linewidth it is possible for the modulations to cause a variation in the widths of the hyperfine lines that is symmetric about the central line of the spectrum but increases monotonically as the wings are approached.<sup>12</sup> It is thus of interest to inquire as to the various reasonable ways in which correlations consistent with the observed linewidth effects in these spectra can arise by means of dynamical rotations or solvent interactions, and the present paper is devoted to this subject.

We consider a variety of dynamical models and emphasize their form or symmetry to show how the required correlations may result rather than attempt to obtain quantitative parameters for the models. A detailed quantitative determination of the parameters for the different radical species would be difficult and at best highly approximate, while the present treatment should establish a framework independent of such approximate calculations upon which further experimental and theoretical work can be built.

The dynamical rotations or solvent interactions can cause two types of correlations in the fluctuations of the hyperfine splittings. One results from an actual correlation of the dynamical motions of the different substituents and the other from a redistribution of the electron spin density throughout the radical. Correlations of the latter type can result from the rotation or solvation at even a single site in the radical, and may, of course, be caused directly in multisubstituted species by correlations of the dynamical motions as well. The motions are investigated in terms of classical models based upon Brownian rotatory diffusion and also as a series of random jumps<sup>15</sup> between discrete states. Emphasis is placed on substituted benzene radicals.

In Sec. II, those portions of the general theory of linewidths relevant to the present paper are summarized, and a general discussion of the way in which rotations of substituents affect the hyperfine interactions is given in Sec. III. The effects of the motions of coupled and uncoupled rotors are discussed in Sec. IV, where spin-density redistributions are neglected and only the Brownian motion models for free rotors and torsional oscillators are employed. In Sec. V the effects of spin-density redistributions throughout the radical are included, and in Sec. VI appropriate discrete jump models are analyzed.

## II. GENERAL THEORY

According to the recently developed theory, the linewidths in the ESR spectra of free radicals in solution<sup>12</sup> are given by the eigenvalues of a relaxation matrix. The elements of this matrix are linear combinations

<sup>15</sup> We use the term "jump" to distinguish motions in which there are only a small number of distinguishable sites from those with a continuous distribution of sites. The latter are referred to as "Brownian motion" models.

of certain spectral densities  $j_{ij}^{(\mu)}(\omega)$  that are in turn functions of the line broadening and relaxation mechanisms. In these symbols for the spectral densities, the frequency  $\omega/2\pi$  is the transition frequency for that part of the perturbation which is associated with the particular spectral density, the type of perturbation is indicated by the superscript  $(\mu)$ , and the nuclei involved are denoted by subscripts ( $i$  and  $j$ ). For mechanisms which modulate the isotropic hyperfine interactions,

$$j_{ij}^{(I)}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} g_{ij}^{(I)}(\tau) \exp(-i\omega\tau) d\tau, \quad (2.1)$$

where the correlation function  $g_{ij}^{(I)}(\tau)$  is

$$g_{ij}^{(I)}(\tau) = \gamma_e^2 \langle [a_i(t) - \bar{a}_i][a_i(t+\tau) - \bar{a}_i] \rangle. \quad (2.2)$$

The angular brackets indicate a time average over the fluctuating splittings;  $a_i(t)$  is the instantaneous hyperfine splitting arising from the contact interaction with nucleus  $i$  at time  $t$ ;  $\bar{a}_i = \langle a_i(t) \rangle$  is its time-average value; and  $\gamma_e$  is the magnetogyric ratio of the electron. The splittings of the lines in the spectrum (in gauss) are determined by  $\bar{a}_i$ . The correlation functions frequently vary exponentially with the time, or are a sum of exponential terms

$$g_{ij}^{(I)}(\tau) = \sum_n K_{ij,n} \exp(-\tau/\tau_n), \quad (2.3)$$

where  $K_{ij,n}$  is independent of time, so that

$$j_{ij}^{(I)}(\omega) = \sum_n K_{ij,n} [\tau_n / (1 + \omega^2 \tau_n^2)]. \quad (2.4)$$

In general the relaxation matrix is not diagonal, and it must be diagonalized by explicit calculation for each particular problem. The off-diagonal matrix elements are of two types, pseudosecular and nonsecular. The former arise from nuclear-spin transitions ( $\omega \cong 0$ ), and the latter from electron-spin transitions ( $\omega \cong \omega_0$ , where  $\omega_0/2\pi$  is the Larmor frequency of the ESR experiment) with or without an accompanying nuclear-spin transition. The nonsecular contributions are often small: At  $X$ -band frequencies it follows from Eq. (2.4) that they are less than 5% of the secular ( $\omega = 0$ ) and pseudosecular terms if  $\tau_n \geq 0.75 \times 10^{-10}$  sec. Note also that since for small values of the correlation time  $\tau_n$ ,  $j_{ij}^{(\mu)}(\omega)$  is proportional to  $\tau_n$ , a mechanism with a very small value of  $\tau_n$  often makes only an insignificant contribution. The nonsecular terms can therefore ordinarily be neglected, and they are not included in most of the linewidth expressions given in the following. The pseudosecular contributions arise from the anisotropic intramolecular dipolar and quadrupole interactions, and for the former they are comparable in magnitude to the secular contributions. There are no pseudosecular contributions from modulations of the isotropic splittings.

When the secular contributions from modulations of the isotropic hyperfine splittings are the predominant

source of line broadening, so that the off-diagonal pseudosecular terms are small, the relaxation matrix can be adequately approximated by only its diagonal elements. For this reason, as well as for simplicity, we only give formulas for the contribution of the modulation of the isotropic splittings to the diagonal elements of the principal part<sup>12</sup> of the relaxation matrix. More generally, the pseudosecular and/or nonsecular terms cannot be neglected, and the other elements of the matrix must be obtained and the diagonalization carried out.

Degenerate absorption lines require special attention. A degenerate line consists of a number of transitions between different quantum states, and it is the widths of these individual transitions between pairs of states that are given by the eigenvalues of the relaxation matrix. For radicals tumbling rapidly in solution, these individual transitions are of Lorentzian shape,<sup>12,16</sup> but since the widths of the individual transitions involved in a degenerate line may be different, the superposition of Lorentzian-shaped components that gives the overall experimentally observable absorption is not in general of Lorentzian shape.<sup>12,17</sup> When the differences among the widths of the individual components are large, it is not possible to obtain an expression for the over-all width in closed form, and the width must be determined numerically by superimposing the individual Lorentzian-shaped components.<sup>17</sup> On the other hand, if the differences among the widths of the components are small, the over-all shape reduces to a Lorentzian with a width determined by the average of the component widths,<sup>12</sup> in agreement with the result given by Kivelson.<sup>9</sup>

With the approximations indicated above, the contribution to the component widths from modulations of the isotropic interaction can be expressed quite simply: For the  $i$ th component of the  $k$ th line, Eq.

$$[T_{2,i}^{(k)}(I; \text{sec.})]^{-1} = \sum_r \{ j_{rr}^{(l)}(0) M_r^2 + \sum_{u \neq v} [j_{ru}^{(l)}(0) - j_{rv}^{(l)}(0)] M_{r_u} M_{r_v} \} + \sum_{r \neq s} \sum_{u,v} j_{ru}^{(l)}(0) M_{r_u} M_{s_v}, \quad (2.7)$$

where

$$M_r = \sum_{u \text{ in } r} M_{r_u} = \sum_{i \text{ in } r} m_i. \quad (2.8)$$

Let us first consider the lines arising from only one group of equivalent nuclei, i.e., the  $r$ th term of the first line of Eq. (2.7). If the nuclei in this group are all completely equivalent,  $j_{ru}^{(l)}(0) = j_{rv}^{(l)}(0)$ , and the linewidth varies as  $M_r^2$ . Each component of a degenerate line then has the same width, and the lines are Lorentzian. On the other hand, in the limit that  $j_{ru}^{(l)}(0) = -j_{rv}^{(l)}(0)$  for  $u \neq v$ , as can often happen (see below), the different hyperfine lines are in general

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$$[T_{2,i}^{(k)}(I; \text{sec.})]^{-1} = \sum_{i,j} j_{ij}^{(l)}(0) m_i m_j = \sum_{r_u, s_v} j_{r_u, s_v}^{(l)}(0) M_{r_u} M_{s_v}, \quad (2.5)$$

where  $m_i$  is the  $z$  component of the spin angular momentum of the  $i$ th nucleus. In the expression on the right, the nuclei have been collected into equivalent groups. Two nuclei are called *equivalent* if the zero-order Hamiltonian is invariant to an interchange of their positions, and they are called *completely equivalent* if the total Hamiltonian is invariant to this interchange. The total Hamiltonian is the sum of the perturbing Hamiltonian which causes line broadening and relaxation and of the zero-order Hamiltonian. The latter is the time average of the total Hamiltonian, and its eigenvalues determine the positions of the lines in the spectrum. We exclude cases of accidental rather than symmetrical equivalence.<sup>12</sup> The quantum number  $M_{r_u}$  is the sum of the  $z$  components  $m_i$  of the nuclear-spin angular momenta of the nuclei in the  $u$ th completely equivalent subgroup of the  $r$ th equivalent group,

$$M_{r_u} = \sum_{i \text{ in } r_u} m_i, \quad (2.6)$$

and similarly  $M_{s_v}$  is the sum over nuclei in the  $v$ th completely equivalent subgroup of the  $s$ th equivalent group. The second summation in Eq. (2.5) is over all equivalent groups  $r$  and  $s$ , over all completely equivalent subgroups  $u$  in  $r$ , and over all completely equivalent subgroups  $v$  in  $s$ . If nuclei  $i$  and  $j$  are in the same completely equivalent subgroup  $r_u$ ,  $j_{ij}^{(l)}(0) = j_{ji}^{(l)}(0) = j_{ij}^{(l)}(0) = j_{ru}^{(l)}(0)$ , and for a symmetrically equivalent group  $r$ ,  $j_{ru}^{(l)}(0) = j_{rv}^{(l)}(0) = j_{rr}^{(l)}(0)$ , but  $j_{ru}^{(l)}(0) \neq j_{rv}^{(l)}(0)$  if  $r_u$  and  $r_v$  are different subgroups. Equation (2.5) can thus be written as

the superposition of components of different widths, and linewidth anomalies such as the alternating linewidth phenomenon occur.<sup>1-7,13</sup> In intermediate cases, there is a mixture of the quadratic and alternating types of dependence of the widths on the quantum numbers  $M_r$ . One other simple special case which is sometimes important is that of an equivalent group of nuclei for which the different completely equivalent subgroups of nuclei are uncorrelated with each other, i.e.,  $j_{ru}^{(l)}(0) = 0$  for  $u \neq v$ . For a single equivalent group  $r$ , Eq. (2.5) then becomes (whether or not  $r$  is a symmetrically equivalent group)

$$[T_{2,i}^{(k)}(I; \text{sec.})]_r^{-1} = \sum_u j_{ru}^{(l)}(0) M_{r_u}^2. \quad (2.9)$$

Examples of these results are given in I for two nuclei

<sup>16</sup> R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

<sup>17</sup> J. Gendell, J. H. Freed, and G. K. Fraenkel, J. Chem. Phys. **41**, 949 (1964).

TABLE I. Secular linewidths, modulation of isotropic hfs, four, eight, and 12 equivalent protons in two completely equivalent subgroups.

No. of protons	$M^a$	$(M_1, M_2)^{a,b}$	Degeneracies		$[T_{2,s}^{(k)}(I; \text{sec.})]^{-1}$	
			$D_i$	$D_M$	General	Out-of-phase correlated $j_{12} = -j_{11}$
4	$\pm 2$	$\pm 1, \pm 1$	1	1	$4j_{11} - 2(j_{11} - j_{12})$	0
	$\pm 1$	$(\pm 1, 0)$	4	4	$j_{11}$	$j_{11}$
	0	$(\pm 1, \mp 1)$	2	6	$0 + 2(j_{11} - j_{12})$	$4j_{11}$
		0, 0	4		0	0
8	$\pm 4$	$\pm 2, \pm 2$	1	1	$16j_{11} - 8(j_{11} - j_{12})$	0
	$\pm 3$	$(\pm 2, \pm 1)$	8	8	$9j_{11} - 4(j_{11} - j_{12})$	$j_{11}$
	$\pm 2$	$(\pm 2, 0)$	12	28	$4j_{11}$	$4j_{11}$
		$\pm 1, \pm 1$	16		$4j_{11} - 2(j_{11} - j_{12})$	0
	$\pm 1$	$(\pm 2, \mp 1)$	8	56	$j_{11} + 4(j_{11} - j_{12})$	$9j_{11}$
		$(\pm 1, 0)$	48		$j_{11}$	$j_{11}$
	0	$(\pm 2, \mp 2)$	2		$0 + 8(j_{11} - j_{12})$	$16j_{11}$
		$(\pm 1, \mp 1)$	32		$0 + 2(j_{11} - j_{12})$	$4j_{11}$
	0, 0	36		0	0	
12	$\pm 6$	$\pm 3, \pm 3$	1	1	$36j_{11} - 18(j_{11} - j_{12})$	0
	$\pm 5$	$(\pm 3, \pm 2)$	12	12	$25j_{11} - 12(j_{11} - j_{12})$	$j_{11}$
	$\pm 4$	$(\pm 3, \pm 1)$	30	66	$16j_{11} - 6(j_{11} - j_{12})$	$4j_{11}$
		$\pm 2, \pm 2$	36		$16j_{11} - 8(j_{11} - j_{12})$	0
	$\pm 3$	$(\pm 3, 0)$	40	220	$9j_{11}$	$9j_{11}$
		$(\pm 2, \pm 1)$	180		$9j_{11} - 4(j_{11} - j_{12})$	$j_{11}$
	$\pm 2$	$(\pm 3, \mp 1)$	30	495	$4j_{11} + 6(j_{11} - j_{12})$	$16j_{11}$
		$(\pm 2, 0)$	240		$4j_{11}$	$4j_{11}$
	$\pm 1$	$\pm 1, \pm 1$	225		$4j_{11} - 2(j_{11} - j_{12})$	0
		$(\pm 3, \mp 2)$	12	792	$j_{11} + 12(j_{11} - j_{12})$	$25j_{11}$
		$(\pm 2, \mp 1)$	180		$j_{11} + 4(j_{11} - j_{12})$	$9j_{11}$
	0	$(\pm 1, 0)$	600		$j_{11}$	$j_{11}$
$(\pm 3, \mp 3)$		2	924	$0 + 18(j_{11} - j_{12})$	$36j_{11}$	
$(\pm 2, \mp 2)$		72		$0 + 8(j_{11} - j_{12})$	$16j_{11}$	
$(\pm 1, \mp 1)$		450		$0 + 2(j_{11} - j_{12})$	$4j_{11}$	
	0, 0	400		0	0	

<sup>a</sup>  $M = M_1 + M_2$ , where  $M_1$  refers to one completely equivalent subgroup of protons and  $M_2$  to the other.

<sup>b</sup> Parentheses indicate that the state specified by  $(M_1, M_2)$  and also the state obtained by permutation of 1 and 2,  $(M_2, M_1)$ , are both included.

of spins  $\frac{1}{2}$ , 1, and  $\frac{3}{2}$  (Table II), and in the case of a special type of modulation, for four protons and four methyl groups (Table IV). Three other simple situations which will be useful in later sections are given here in Table I. Linewidths are listed for examples with four, eight, and 12 equivalent protons having the nuclei grouped into two different completely equivalent

sets containing two, four, and six protons, respectively. The four-proton case is applicable to the *p*-dinitrobenzene anion,<sup>18</sup> and the eight-proton case to the pyracene anion.<sup>7</sup> The 12-proton example corresponds to four methyl groups in two completely

<sup>18</sup> J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **40**, 1815 (1964).

equivalent subgroups, and is thus applicable to the dinitrodurene anion.<sup>2,5,19</sup> This table shows that when the modulation is correlated to be completely out of phase ( $j_{12} = -j_{11}$ ), and when  $j_{11}$  makes a large contribution to the linewidths, alternate lines in these spectra are broad (width  $j_{11}$  or greater) and the intervening lines are narrow (at least one component with a zero linewidth contribution from this mechanism). Of course, if  $j_{12} = -j_{11}$  and  $j_{11}$  is very large, the intensity distribution would be abnormal. As an example, for the eight equivalent protons, the sharp lines would correspond to  $M = \pm 4, \pm 2,$  and  $0,$  and would have statistical weights  $1:16:36:16:1$  whereas in a spectrum with  $j_{12} = j_{11}$ , all nine lines would be observed and the statistical weights would be  $1:8:28:56:28:8:1.$

When there is more than one group of equivalent nuclei, each of the groups has linewidths governed by the first line of Eq. (2.7), but in addition there are cross terms arising from the second line of the equation. It is sometimes possible to approximate the cross terms by contributions of the form  $j_{rs}^{(2)}(0)M_r M_s$ , i.e., omitting distinctions between different subgroups, so that the cross term adds a linewidth variation, which, for constant  $M_s$ , is a linear function of  $M_r$ . Thus if  $M_s$  can take on the value zero, there are lines in the spectrum for which there are no linewidth contributions from the cross terms.<sup>18</sup> In certain simple cases these variations lead to interesting information such as the relative signs of the isotropic hyperfine splittings,<sup>5,18,20</sup> but more generally there is an appreciable linewidth effect attributable to the cross terms which causes complicated linewidth variations.

The formulation we have used<sup>12</sup> is based on the relaxation matrix theory<sup>21-24</sup> and is limited to rapid modulations in the sense that the correlation time of modulating motion  $\tau_c$  and the magnitude of the perturbing Hamiltonian  $\hbar\mathcal{H}_1(t)$  must satisfy the condition  $[\langle |\mathcal{H}_1|^2 \rangle_M \tau_c^2]^{1/2} \ll 1$ . Thus if a modulating mechanism causes fluctuations in the isotropic hyperfine splitting of an amount  $\Delta a$  gauss, the theory only holds if  $|\gamma_e| |\Delta a| \tau_c \ll 1$ . When this inequality does not hold, it is still possible in certain circumstances to treat the linewidth variations by using either the modified form of the Bloch equations<sup>25</sup> or the Anderson theory of motional narrowing,<sup>26</sup> two procedures that are essentially equivalent in this application. They are normally

<sup>19</sup> J. H. Freed and G. K. Fraenkel, *J. Am. Chem. Soc.* **86**, 3477 (1964).

<sup>20</sup> B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.* **41**, 695 (1964).

<sup>21</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

<sup>22</sup> A. G. Redfield, *IBM J. Res. Develop.* **1**, 19 (1957).

<sup>23</sup> F. Bloch, *Phys. Rev.* **102**, 104 (1956).

<sup>24</sup> Y. Ayant, *J. Phys. Rad.* **16**, 411 (1955).

<sup>25</sup> F. Bloch, *Phys. Rev.* **70**, 460 (1946); J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959); H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.* **21**, 279 (1953); H. M. McConnell, *ibid.* **28**, 430 (1958).

<sup>26</sup> P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954).

limited to mechanisms which involve discrete jumps<sup>16</sup> from one site to another and thus do not readily provide a means of formulating the linewidth variations caused by continuous motions. Only secular effects can be treated,<sup>12,27</sup> and in practice it is not possible to handle problems involving more than a small number of jumps.<sup>13</sup>

### III. MOTIONAL MODULATIONS OF THE HYPERFINE SPLITTINGS

Several different types of modulations of the isotropic hyperfine splittings which are of importance have been mentioned in the introduction. One of these involves rotations of substituent groups on an aromatic ring like a nitro group, and in this section we first consider in a general way how the hyperfine splittings are affected by such rotations. We then discuss the models available for describing the time dependence of this and other modulations of the hyperfine splittings.

The substituents we wish to consider are nitro ( $-\text{NO}_2$ ), carboxylate ( $-\text{COO}^-$ ), hydroxyl ( $-\text{OH}$ ), formyl ( $-\text{CHO}$ ), acetyl ( $-\text{COCH}_3$ ), amino ( $-\text{NH}_2$ ), etc. Methyl groups are treated elsewhere.<sup>19</sup> These groups tend to conjugate with the pi system of the radical, and the most stable conformations are normally ones in which the plane of the substituent coincides with the plane of the aromatic ring. If there are bulky neighboring substituents, however, the equilibrium orientation may not be in the plane of the aromatic ring, and the instantaneous orientation may be affected both by intramolecular and intermolecular interactions. Some of the crowding effects of substituents are quite marked. Thus x-ray studies show that while nitrobenzene is planar,<sup>28</sup> the nitro group in nitromesitylene<sup>29</sup> (1-nitro-2,4,6-trimethylbenzene) is twisted out of the plane by  $66.4^\circ$ . The orientation of the substituent may alter the hyperfine splitting of nuclei in the substituent directly, even without affecting the spin-density distribution, but in general the spin density in the group and throughout the molecule depends on the orientation. Thus Geske and co-workers<sup>30,31</sup> have found that the  $^{14}\text{N}$  splittings in methyl-substituted nitrobenzene anions increase with the degree of steric hindrance in the neighborhood of the nitro group while the splittings at other positions in the radicals decrease.

The variation of the spin-density distribution and hyperfine splittings with the angle of orientation  $\theta$  of a substituent can be expressed as a Fourier series in  $\theta$ . If there is only a single substituent attached to a planar pi-electron system, the Fourier series must be an even function of the angle  $\theta$  (where  $\theta$  is zero when the substituent is in the plane of the aromatic system) and

<sup>27</sup> J. I. Kaplan, *J. Chem. Phys.* **28**, 278 (1958); **29**, 462 (1958); I. Solomon and N. Bloembergen, *ibid.* **25**, 261 (1956).

<sup>28</sup> J. Trotter, *Acta Cryst.* **12**, 884 (1959).

<sup>29</sup> J. Trotter, *Acta Cryst.* **12**, 605 (1959).

<sup>30</sup> D. H. Geske and J. Ragle, *J. Am. Chem. Soc.* **83**, 3532 (1961).

<sup>31</sup> D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.* **86**, 987 (1964).

we assume this to be true as well for aromatic radicals with more than one substituent. Although even functions of  $\theta$  may not be sufficient for the description of all multisubstituted systems, as for example the *o*-dinitrobenzene anion, the inclusion of the more general Fourier series presents no fundamental difficulty but does add considerable algebraic complexity. We therefore consider for simplicity Fourier series which contain only cosine terms. The instantaneous value of the pi-electron spin density at the point  $i$  in a radical with several rotating substituents at orientations  $\theta_1, \theta_2, \dots$ , can consequently be written

$$\begin{aligned} \rho_i^\pi(t) = & \alpha_i + \sum_{n=1}^{\infty} \beta_{i;n} \cos n\theta_1 + \sum_{n=1}^{\infty} \gamma_{i;n} \cos n\theta_2 + \dots \\ & + \sum_{n,m=1}^{\infty} \delta_{i;nm} \cos n\theta_1 \cos m\theta_2 + \dots \\ & + \sum_{n,m,l=1}^{\infty} \epsilon_{i;nml} \cos n\theta_1 \cos m\theta_2 \cos l\theta_3 + \dots \quad (3.1) \end{aligned}$$

Higher-order correlations must be included for radicals with more than three rotors. For groups with a twofold symmetry axis such as  $-\text{NO}_2$ ,  $-\text{COO}^-$ , or  $-\text{NH}_2$ , only even harmonics contribute to the series ( $\cos 2n\theta_i$ ), but for  $-\text{OH}$ ,  $-\text{CHO}$ , and  $-\text{COCH}_3$ , both odd and even harmonics must be included. The spin density at any point along the axis of rotation of these groups without twofold symmetry, however, involves only even harmonics.

For C-H ring protons the isotropic hyperfine splittings are determined by relations like that of McConnell,<sup>32</sup>

$$a_i^{\text{H}} = Q_{\text{CH}}^{\text{H}} \rho_i^\pi \quad (3.2)$$

while for  $^{13}\text{C}$  and  $^{14}\text{N}$  nuclei, etc., Karplus and Fraenkel<sup>33</sup> have shown that the splittings also depend on the spin density on contiguous atoms. The sigma-pi parameters relating splittings to pi-electron spin densities for nuclei not in the rotating groups are presumably constant, but those for nuclei rotating with respect to the rest of the molecule are functions of orientation. For proton splittings in rotating groups such as  $-\text{CHO}$ ,  $-\text{NH}_2$ , or  $-\text{OH}$ , it is readily seen that  $Q_{\text{XH}}^{\text{X}}(\theta)$  (X is C, N, or O) is an even function of  $2\theta$  in the approximation that the orientation of other substituents has a negligible influence on the  $Q$ 's. Here, of course,  $\theta$  is the angle of orientation of the group containing the proton, not some other rotating group in the radical. Similarly, the nitrogen splitting in an  $-\text{NO}_2$  or  $-\text{NH}_2$  group is an even function of  $2\theta$ . The  $Q$ 's can thus be expressed as Fourier cosine series in  $2\theta$ , and in combination with Eq. (3.1) we can write for the instantaneous splitting from

<sup>32</sup> H. M. McConnell, *J. Chem. Phys.* **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.* **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.* **28**, 107 (1958); and other papers cited therein.

<sup>33</sup> M. Karplus and G. K. Fraenkel, *J. Chem. Phys.* **35**, 1312 (1961).

nucleus  $i$

$$\begin{aligned} a_i(t) = & A_i + \sum_{n=1}^{\infty} B_{i;n} \cos n\theta_1 + \sum_{n=1}^{\infty} C_{i;n} \cos n\theta_2 + \dots \\ & + \sum_{n,m=1}^{\infty} D_{i;nm} \cos n\theta_1 \cos m\theta_2 + \dots, \quad (3.3) \end{aligned}$$

plus higher-order terms for more than two rotors, and with appropriate restrictions on the values of  $n, m, \dots$  for the different groups.

Evaluation of the coefficients in Eq. (3.1) requires a detailed knowledge of the effect of the rotational motion on the spin-density distribution. A useful although highly approximate estimate can be obtained from molecular orbital calculations if appropriate assumptions are made about the coupling between the aromatic ring and the substituent, and such calculations have been performed for nitrobenzenes<sup>34</sup> by allowing the resonance integral between the ring and the nitro group to vary as  $|\cos\theta|$ . To obtain the coefficients in Eq. (3.3) it is also necessary to estimate the variation of the sigma-pi parameters ( $Q$ 's) with orientation. For our present purposes, however, it is sufficient to formulate the linewidth variations as functions of the parameters  $A_i, B_{i;n}$ , etc., in the Fourier series, and to deduce the general nature of the linewidth effects rather than to resort to specific and necessarily highly approximate models.

In general the time dependence of the hyperfine splittings arising either from rotation of the substituents as expressed by Eq. (3.3), or from the formation of fluctuating solvent complexes at particular sites in the radical, causes a nonvanishing correlation function  $g_{ij}(\tau)$  [Eq. (2.2)] both for a nucleus with itself ( $g_{ii}$ ) and for different nuclei with each other ( $g_{ij}, i \neq j$ ). In addition, a coupled motion of two rotating groups introduces a source of correlation of the splittings from nuclei in different rotors, and if solvation at two different sites is correlated, so are the splittings. The coupled motion of two rotors is likely to occur in highly hindered polysubstituted compounds such as dinitro- or dihydroxydurene. If, for example, one nitro group in dinitrodurene were in the plane of the benzene ring, the methyl groups would probably be distorted in such a way as to crowd the second nitro group out of the plane. A correlated jump would also be expected in the naphthazarin cation<sup>3</sup>: when the proton between two neighboring oxygen atoms jumps to a position at one side of the oxygen atoms, the proton that was originally on the other side probably jumps into the central position vacated by the first proton.

The mechanical model for the modulating motion is difficult to specify in detail. For discrete jump motions of the type that are probably appropriate for the naphthazarin cation<sup>3</sup> or the pyracene anion,<sup>7</sup> it is customary to assume that the time elapsed in the course of a jump from one site to another is short, and only

<sup>34</sup> P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.* **39**, 609 (1963).

the lifetimes and splittings for the different states have to be known to determine the correlation functions. A specification of the states and lifetimes implicitly includes any possible correlations between the motions at different sites. Discrete jump models<sup>15</sup> can also be employed for rotating groups<sup>1,2,12</sup> but they are rather restrictive. Thus, each nitro group in the dinitroarene anion might be assumed to have only two conformations, one in the plane of the ring and one perpendicular to the plane, so that jumps would take place between the four states corresponding to the two different orientations of each nitro group. Certainly the most appropriate description of the rotational motions for the isolated molecule would be along the lines of the quantum-mechanical treatment of hindered internal rotation, and would include the possibilities of tunneling through potential barriers. In solutions, the effect of solvent interactions might then be included as a time-dependent perturbation causing random transitions among the stationary-state energy levels of the hindered rotor, but it is difficult to perform such a calculation in a meaningful way. The rotational motion could also be described classically, and the effects of the solvent interactions treated by the theory of Brownian motion, but the validity of this approach is also open to question because the spacing of the energy levels of the internal motion in the isolated molecule is probably not small compared to  $kT$ . Nevertheless, we use the classical theory of Brownian motion for simplicity, and can anticipate that meaningful although not quantitatively significant results will be obtained.

The actual solution of the Langevin equation for the Brownian motion<sup>35</sup> of a particle subject to the multiple-minimum potential energy appropriate for a description of hindered internal rotation is, unfortunately, also a difficult mathematical problem.<sup>36</sup> As a result, we have approximated the motion by a variety of physically somewhat unrealistic models that represent limiting cases. The detailed models employed are described in the following sections.

The correlation functions defined in Eq. (2.2) are determined for the Brownian-motion models by conditional probability distributions which are given in Appendix A. For the jump models, the conditional probabilities are obtained from solving a set of coupled first-order linear differential equations. These equations can be written down by inspection using the usual arguments of chemical kinetics, but when many states are involved, their solution is difficult. A few cases have been solved in I, and another is presented in Appendix B. In the approximation of small and rapid modulations appropriate for the relaxation-matrix theory of I, the positions of the lines in the spectrum

are determined by the average hyperfine splittings,  $\langle a_i(t) \rangle$ , which, for rotational motions, is the average of Eq. (3.3).

#### IV. BROWNIAN MOTION OF ROTORS NEGLECTING SPIN-DENSITY MODULATIONS

In this section the correlation functions and spectral densities are calculated for specific models of rotating substituents using Brownian motion to treat the dynamics. It is assumed that the motion of a particular rotating group affects only those hyperfine splittings that are from nuclei within this same rotating group, and thus the influence of the rotation on the spin-density distribution throughout the molecule is neglected. This unrealistic assumption is made here in order to focus attention on the motional aspects of the problem in as simple a manner as possible. The inclusion of spin-density variations is undertaken in Sec. V, and discrete jump models<sup>15</sup> are discussed in Sec. VI.

According to the assumptions of this section, the hyperfine splitting  $a_i$  for a nucleus in a rotating group depends only on the orientation  $\theta_i$  of the rotating group and is independent of the orientation  $\theta_j$  ( $i \neq j$ ) of other rotating groups. It also follows that the hyperfine splittings from nuclei that are not in rotating groups are constant and, according to the approximations of Sec. III, only even harmonics are required in the Fourier series. Equation (3.3) is thus greatly simplified:

$$a_i(t) = A_i + \sum_{n=1}^{\infty} B_{i;n} \cos 2n\theta_i. \quad (4.1)$$

The Brownian motion of a single rotating group is described either as a free rotational diffusion or as a small torsional oscillation about an equilibrium position. Correlation between two rotors is introduced both as a rigid coupling between the two groups so that they move as a single unit or as a small relative torsional oscillation about an equilibrium separation.

#### A. Correlation Functions and Spectral Densities for Specific Models

##### Case a. Uncorrelated Motion of Rotors Undergoing Free Rotational Diffusion

For free rotational diffusion, using Eqs. (4.1) and (A2), the average splitting is  $\bar{a}_i = A_i$ . The average required to obtain the correlation function  $g_{ii}^{(1)}(\tau)$  involves the sum of terms like

$$\begin{aligned} & \langle \cos 2n\theta_i(t) \cos 2m\theta_i(t+\tau) \rangle \\ &= \int_0^{2\pi} d\theta_{i0} W(\theta_{i0}) \cos 2n\theta_{i0} \int_{-\infty}^{\infty} d\theta_i P(\theta_i | \theta_{i0}, \tau) \cos 2m\theta_i, \\ &= \int_0^{2\pi} W(\theta_{i0}) \cos 2n\theta_{i0} \cos 2m\theta_{i0} \exp(-4m^2 D_i \tau) d\theta_{i0}, \\ &= \frac{1}{2} \exp(-4n^2 D_i \tau) \delta_{nm}, \end{aligned} \quad (4.2)$$

<sup>35</sup> (a) S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943); (b) G. E. Uhlenbeck, and L. S. Ornstein, *Phys. Rev.* **36**, 823 (1930); (c) M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945); (d) S. O. Rice, *Bell System Tech. J.* **23**, 282 (1944); **25**, 46 (1945).

<sup>36</sup> But see M. Goldstein, *J. Chem. Phys.* **39**, 243 (1963), where some preliminary results are discussed.

from Eqs. (A2) and (A3), where  $\delta_{ij}$  is the Kronecker delta. Since according to this model there is no correlation for Nuclei  $i$  and  $j$  in different rotors,  $g_{ij}^{(T)}(\tau) = 0$  ( $i \neq j$ ), and thus

$$g_{ij}^{(T)}(\tau) = \delta_{ij}(\gamma_e^2/2) \sum_{n=1}^{\infty} B_{in}^2 \exp(-4n^2 D_i \tau). \quad (4.3)$$

It follows that

$$j_{ij}^{(T)}(\omega) = \delta_{ij}(\gamma_e^2/2) \sum_{n=1}^{\infty} B_{in}^2 [\tau_{in}(1 + \omega^2 \tau_{in}^2)^{-1}], \quad (4.4)$$

where

$$\tau_{in}^{-1} = 4n^2 D_i. \quad (4.5)$$

Since by assumption there are only uncorrelated motions in this model, the nuclei in different rotating groups are never completely equivalent [here  $j_{ij}^{(T)}(\omega) = 0$ ,  $i \neq j$ , while if  $i$  and  $j$  are completely equivalent nuclei,  $j_{ij} = j_{ii}$ ]. The contribution to the linewidths from the motion is given by Eq. (2.9), and the variation in width from one hyperfine component to another is rather complicated when this contribution is appreciable (see, for example, the last column of Table II in I).

#### Case b. Uncorrelated Motion of Rotors Undergoing Small Torsional Oscillations

For small torsional oscillations, the angles  $\theta_i$  in Eq. (4.1) must be expanded for small displacements

$$y_i = \theta_i - \theta_{ie} \quad (4.6)$$

from the equilibrium position  $\theta_{ie}$ . Thus

$$\cos 2n\theta \cong (1 - 2n^2 y_i^2) \cos 2n\theta_{ie} - 2ny_i \sin 2n\theta_{ie} \quad (4.7)$$

from which, using Eq. (A5), the average hyperfine splitting is

$$\bar{a}_i = A_i + \sum_{n=1}^{\infty} B_{in} [1 - (2n^2 \beta_i D_i / \omega_{i0}^2)] \cos 2n\theta_{ie} \quad (4.8)$$

and

$$a_i(\theta_i) - \bar{a}_i$$

$$= \sum_{n=1}^{\infty} B_{in} [2n^2 (y_i^2 - \langle y_i^2 \rangle_w) \cos 2n\theta_{ie} + 2ny_i \sin 2n\theta_{ie}], \quad (4.9)$$

where [Eq. (A6)]

$$\langle y_i^2 \rangle_w = (\beta_i D_i / \omega_{i0}^2) = (kT / I_i \omega_{i0}^2) \quad (4.10)$$

is the mean-square displacement from equilibrium. The correlation function becomes

$$g_{ij}^{(T)}(\tau) = \delta_{ij} \sum_{n,m} 4B_{in} B_{im} nm [nm \cos 2n\theta_{ie} \cos 2m\theta_{ie} g^{(\theta)}(\tau) + \sin 2n\theta_{ie} \sin 2m\theta_{ie} g^{(\theta)}(\tau)], \quad (4.11)$$

where  $g^{(\theta)}(\tau)$  and  $g^{(\theta^2)}(\tau)$  are given by Eqs. (A8) and (A10), and the spectral density  $j_{ij}^{(T)}(\omega)$  is given by a similar expression with  $j^{(\theta)}(\omega)$  and  $j^{(\theta^2)}(\omega)$  from Eqs. (A9) and (A13) substituted for  $g^{(\theta)}(\tau)$  and  $g^{(\theta^2)}(\tau)$ ,

respectively. Retaining only the leading terms in the Fourier series for  $a_i(t)$ , the spectral density at zero frequency is thus, from Eqs. (A15) and (A16),

$$j_{ij}^{(T)}(0) = \delta_{ij} (4\gamma_e^2 \beta_i^2 D_i B_{i1}^2 / \omega_{i0}^4) [\sin^2 2\theta_{ie} + (D_i / \beta_i \omega_{i0}^2) (\omega_{i0}^2 + \beta_i^2) \cos^2 2\theta_{ie}], \quad (4.12)$$

while for large damping and low frequencies, Eqs. (A17) and (A18) give

$$j_{ij}^{(T)}(\omega) = \delta_{ij} (4\gamma_e^2 \beta_i^2 D_i B_{i1}^2 / \omega_{i0}^4) [(1 + \omega^2 \tau_{i1}^2)^{-1} \sin^2 2\theta_{ie} + (\beta_i D_i / \omega_{i0}^2) (1 + \frac{1}{2} \omega^2 \tau_{i1}^2)^{-1} \cos^2 2\theta_{ie}], \quad (4.13)$$

where, as in Eq. (A19),  $\tau_{i1} = (\beta_i / \omega_{i0}^2)$ . Note the angular dependence in these spectral densities which gives the same results for  $\theta_{ie} = 0, \pm\pi$ , or  $\pm(\pi/2)$ , but values that are different from these when, for example,  $\theta_{ie} = \pm(\pi/4)$ . The dependence of the linewidths on the spectral densities is the same as for Case (a).

#### Case c. Locked Pair of Rotors Undergoing Free Rotational Diffusion as a Unit

We assume that the two rotors undergo free rotational diffusion as a coupled group, and that their orientations always differ by the constant angle  $\alpha_{12} = \theta_1 - \theta_2$ . It is also assumed that there is only one magnetic nucleus in each rotor, and we take the coefficients in the Fourier series, Eq. (4.1), for the two nuclei to be the same,  $A_1 = A_2 = A$  and  $B_{1n} = B_{2n} = B_n$ . Letting

$$y = \theta_i + (-1)^i (\alpha_{12}/2) \quad (4.14)$$

for  $i = 1$  or  $2$ , and since  $\bar{a}_i = \bar{a} = A$ , we have

$$a_i(t) = \bar{a} + \sum_{n=1}^{\infty} B_n [\cos n\alpha_{12} \cos 2ny + (-1)^i \sin n\alpha_{12} \sin 2ny]. \quad (4.15)$$

Calculation of the correlation functions and spectral densities proceeds as in (a) above if the probability functions in Eqs. (A2) and (A3) are used for the distribution in  $y$ , with the result that

$$j_{ij}^{(T)}(\omega) = (\gamma_e^2/2) \sum_{n=1}^{\infty} B_n^2 \cos 2n\alpha_{ij} [\tau_n (1 + \omega^2 \tau_n^2)^{-1}], \quad (4.16)$$

where  $\alpha_{ij}$  is given by Eq. (A20), and

$$\tau_n^{-1} = 4n^2 D_T = 2n^2 D \quad (4.17)$$

from Eqs. (4.5) and (A21). For  $\alpha_{12} = 0$  or  $\pi$ ,  $j_{12}^{(T)}(\omega) = j_{11}^{(T)}(\omega)$ , and the two nuclei are completely equivalent. For  $\alpha_{12} = (\pi/2)$ , the terms in  $j_{11}^{(T)}(\omega)$  and  $j_{12}^{(T)}(\omega)$  for  $n$  even are the same, but those for  $n$  odd have opposite signs. Thus if the first ( $n=1$ ) term is dominant, which is reasonable from both the physical situation and the dependence of successive terms in Eq. (4.16) on  $n^{-2}$ , this coupled motion with  $\alpha_{12} = (\pi/2)$  causes  $j_{12}^{(T)}(\omega) = -j_{11}^{(T)}(\omega)$ . Equation (2.7) for  $T_2^{-1}$  applies, and there is a large alternating linewidth effect if the motional modulation contributes appreciably to the total line-



width (see, for example, Table II of I). Note that in general for this case  $|j_{12}^{(I)}(\omega)| \leq j_{11}^{(I)}(\omega)$ .

*Case d. Locked Pair of Rotors Undergoing Small Torsional Oscillations as a Unit*

In this model two locked rotors execute small vibrations as a unit about an equilibrium position. It differs from Part (c) because the over-all motion of the unit is a vibration, rather than a free rotational diffusion. The two rotors are assumed to be equivalent, and therefore their equilibrium orientations must also be equivalent. This requirement implies that  $\theta_{2e} = \pm\theta_{1e}$  or  $\theta_{2e} = \pi \pm \theta_{1e}$ . The rotors are completely equivalent (equivalent at all instants of time) if  $\theta_{2e} = \theta_{1e}$  or  $\theta_{2e} = \pi + \theta_{1e}$  since we also require that  $\theta_1 - \theta_2$  be constant at every instant. These last conditions do not conform to our model of coupled rotations in a molecule like dinitrofluorene, since they do not correspond to a motion in which the rotation of one group into the plane forces the other group out of the plane, but the conditions  $\theta_{2e} = -\theta_{1e}$  or  $\theta_{2e} = \pi - \theta_{1e}$  do conform to this picture. Proceeding as in Parts (b) and (c) above for the conditions  $\theta_{2e} = -\theta_{1e}$  or  $\theta_{2e} = \pi - \theta_{1e}$  results in Eq. (4.8) for the average hyperfine splitting, and gives for the spectral density

$$j_{ij}^{(I)}(\omega) = 4\gamma_e^2 \sum_{n,m} B_n B_m n m [(-1)^{i+j} \sin^2 2n\theta_{ie} j^{(0)}(\omega) + nm \cos^2 2n\theta_{ie} j^{(2)}(\omega)], \quad (4.18)$$

where  $i=1, 2$  and  $j=1, 2$ . The spectral densities  $j^{(0)}(\omega)$  and  $j^{(2)}(\omega)$  are given by Eqs. (A9) and (A13) but with  $D_T = \frac{1}{2}D$  replacing the diffusion constant  $D$ . For the conditions  $\theta_{2e} = \theta_{1e}$  or  $\theta_{2e} = \pi + \theta_{1e}$ , Eq. (4.18) still holds if the coefficient  $(-1)^{i+j}$  is replaced by  $+1$ , and thus as expected  $j_{12}^{(I)}(\omega) = j_{11}^{(I)}(\omega)$ . For the conditions  $\theta_{2e} = -\theta_{1e}$  or  $\theta_{2e} = \pi - \theta_{1e}$  when  $\theta_{1e} = 0, \pi/2$ , or  $\pi$  the equilibrium separations of the two rotors are  $\alpha_{12} = 0$  or  $\pi$ , and the nuclei are completely equivalent [ $j_{12}^{(I)}(\omega) = j_{11}^{(I)}(\omega)$ ]. If  $\theta_{1e} = (\pi/4)$ , corresponding to  $\alpha_{12} = \pm(\pi/2)$ , the dominant terms ( $n=m=1$ ) again lead to  $j_{12}^{(I)}(\omega) = -j_{11}^{(I)}(\omega)$ , and a large alternating linewidth effect can result.

*Case e. Small Relative Oscillations of Two Rotors*

If the two rotors have the same equilibrium positions,  $\theta_{2e} = \theta_{1e}$ , but move in opposite directions,  $(\theta_2 - \theta_{2e}) = -(\theta_1 - \theta_{1e})$ , Eq. (4.18) is again obtained.

*Case f. Pair of Rotors Coupled Together by Harmonic Restoring Force and Undergoing Over-All Free Rotational Diffusion as a Unit*

In this model the two rotors undergo free rotational diffusion as a unit, as in Part (c) above, but they also execute small torsional oscillations with frequency  $\omega_{12}/2\pi$  about an equilibrium separation  $\alpha_e$ . For simplicity we retain only the leading terms in the Fourier expansion ( $n=1$ ). Using the variables  $u_1$  and  $u_2$  of Eqs.

(A23), with  $u_1$  corresponding to the rotational diffusion of the whole group ( $r=1$ ) and  $u_2$  to the torsional oscillations, we can write for small displacements  $u_2$ ,

$$a_i(t) \cong \bar{a} + B_1 \{ [\cos 2u_1 \cos \alpha_e - (-1)^i \sin 2u_1 \sin \alpha_e] (1 - 2u_2^2) - [\cos 2u_1 \sin \alpha_e - (-1)^i \sin 2u_1 \cos \alpha_e] (2u_2) \}, \quad (4.19)$$

where  $i=1$  or  $2$ . Note that the rotors are assumed to be identical and the average of the coefficient of  $B_1$  is zero. The integral for the correlation function is

$$g_{ij}^{(I)}(\tau) = \gamma_e^2 \int_0^{2\pi} du_{10} \int_{-\infty}^{\infty} du_{20} W(u_{10}) W(u_{20}) [a_i(u_{10}, u_{20}) - \bar{a}_i] \times \int_0^{2\pi} du_1 \int_{-\infty}^{\infty} du_2 P(u_{10} | u_{1T}\tau) P(u_{20} | u_{2T}\tau) [a_j(u_1, u_2) - \bar{a}_j], \quad (4.20)$$

where  $W(u_{10})$  and  $P(u_{10} | u_{1T}\tau)$  are given by Eqs. (A2) and (A3) (free rotational diffusion) and  $W(u_{20})$  and  $P(u_{20} | u_{2T}\tau)$  by Eqs. (A5) and (A7) (damped torsional oscillation). In both sets of distribution functions,  $D$  must be replaced by  $D_T = \frac{1}{2}D$ , and in the second set the resonant frequency  $\omega_0$  must be replaced by  $\sqrt{2}\omega_{12}$  [see Eqs. (A25) to (A27)]. We do not consider the case of arbitrary damping of the torsional motion. The results for the spectral densities for large damping are

$$j_{ij}^{(I)}(\omega) = (\gamma_e^2/2) B_1^2 \cos 2\alpha_{ij} \times \{ (1 - 2q^2 + q^4) [\tau_0(1 + \omega^2\tau_0^2)^{-1}] + (-1)^{i+j} 2q^2 [\tau_1(1 + \omega^2\tau_1^2)^{-1}] + 2q^4 [\tau_2(1 + \omega^2\tau_2^2)^{-1}] \}, \quad (4.21)$$

where

$$\begin{aligned} \tau_0^{-1} &= 2D, \\ \tau_1^{-1} &= 2D[1 + \frac{1}{2}q^{-2}], \\ \tau_2^{-1} &= 2D[1 + q^{-2}], \end{aligned} \quad (4.22)$$

with

$$q^2 = (\beta D/2\omega_{12}^2) = (kT/2I\omega_{12}^2), \quad (4.23)$$

and  $\alpha_{12} = \alpha_e$ ,  $\alpha_{11} = \alpha_{22} = 0$ . This result holds only for  $\beta \gg 4\omega_{12}$  and  $\omega \ll \sqrt{2}\omega_{12}$ . For  $q^2 \ll 1$ , corresponding to  $2I\omega_{12}^2 \gg kT$  or very strong coupling of the two rotors, Eq. (4.21) reduces to the leading term of Eq. (4.16) for Case (c), as expected. Except when  $q$  is vanishingly small, the term in  $\tau_1$  causes  $|j_{12}^{(I)}(\omega)| < j_{11}^{(I)}(\omega)$  for all equilibrium separations  $\alpha_e$ , and the two nuclei are never completely equivalent. Unlike the previous models for correlated motion, the present case does not give complete "in-phase correlation" [ $j_{12}^{(I)}(\omega) = j_{11}^{(I)}(\omega)$ ] or complete "out-of-phase correlation" [ $j_{12}^{(I)}(\omega) = -j_{11}^{(I)}(\omega)$ ]. An alternation in linewidth occurs, the greatest effect taking place when  $\alpha_e = (\pi/2)$ , corresponding to the minimum value of  $j_{12}^{(I)}(\omega)$ , but since  $|j_{12}^{(I)}(\omega)| < j_{11}^{(I)}(\omega)$ , the magnitude of the linewidth

alternation is less than for models which give  $j_{12}^{(T)}(\omega) = -j_{11}^{(T)}(\omega)$ .

### B. Comparison of Different Models

All of the Brownian-motion diffusion models in which the motions of the two rotors are correlated can give rise to an alternation in linewidth. If the two rotors are locked together and as a unit undergo either free rotational diffusion or small torsional oscillations about an equilibrium position [Models (c) and (d)], the maximum alternating linewidth effect occurs when the two rotors are perpendicular to each other. In the oscillating case, they must also make an angle of  $45^\circ$  to the plane of the pi system for the maximum alternating effect. The spectral densities then satisfy the relation  $j_{12}^{(T)}(\omega) = -j_{11}^{(T)}(\omega)$  if only leading terms are retained in the Fourier series expansion for the hyperfine splitting as a function of the angle of orientation. This condition is also satisfied if the two rotors have the same equilibrium conformation but are oscillating relative to each other provided the equilibrium conformation is  $45^\circ$  out of the plane of the pi system [Model (e)]. The condition is only approximately satisfied [ $j_{12}^{(T)}(\omega) \approx -j_{11}^{(T)}(\omega)$ ] if the two rotors are oscillating relative to each other with a low enough frequency ( $\omega_{12}$ ) to affect the spectral densities and also at the same time undergoing free rotational diffusion as a unit [Model (f)]. The equilibrium angle of separation of  $90^\circ$ , corresponding to the minimum value of  $j_{12}^{(T)}(\omega)$ , still gives the largest linewidth alternation attainable from this model. The characteristic feature of all these coupled motions is that the alternating linewidth effect is a maximum when the variation of the hyperfine splittings from the nuclei in the two rotors is out of phase, while no alternation in linewidth is produced if their motions are in phase. In general, the inclusion of higher terms in the Fourier series expansion reduces the magnitude of the alternating linewidth effect.

### V. BROWNIAN MOTION OF ROTORS INCLUDING SPIN-DENSITY MODULATIONS

In this section we extend the treatment of Sec. IV by including the effects of modulations of the pi-electron spin-density distribution by the rotational motion. The general Fourier series for  $a_i(t)$ , Eq. (3.3), must now be employed, and the presence of terms like  $\cos n\theta_1 \cos m\theta_2$  causes considerable algebraic complexity. We therefore use only restricted forms of the series, and only two of the models considered in Sec. IV. These are Cases (a) and (c), i.e., the free rotational diffusion of uncorrelated rotors, and a pair of interlocked rotors undergoing free rotational diffusion as a unit. The coefficients in the Fourier series for the different nuclei are interrelated by symmetry in typical cases, and it is convenient to treat the linewidth variations for nuclei in the rotating groups separately from those at other positions in the radicals. The general expressions

for the correlation functions are developed first, then examples are given for the splittings of nuclei in the rotating groups, and finally we consider examples of splittings from ring and methyl-group protons. In the cases worked out, the correlation functions have the form of Eq. (2.3), and since the spectral densities can therefore be obtained from Eq. (2.4), only the correlation functions are given.

#### i. Correlation Functions

##### Case a. Uncorrelated Motion of Rotors Undergoing Free Rotational Diffusion

For simplicity we give the results for only two rotors, and they are assumed to have the same average hyperfine splitting  $\bar{a}_i = A$  and the same rotational diffusion constants  $D$ . From Eqs. (3.3), (A2), and (A3), with the methods of Sec. IV, and with  $i=1$  or  $2$ , we have

$$g_{ij}^{(T)}(\tau) = (\gamma_e^2/2) \left[ \sum_{n=1}^{\infty} (B_{i;n} B_{j;n} + C_{i;n} C_{j;n}) \exp(-\tau/\tau_n) + \frac{1}{2} \sum_{n,m=1}^{\infty} D_{i;nm} D_{j;nm} \exp(-\tau/\tau_{nm}) \right], \quad (5.1)$$

where

$$\tau_n^{-1} = n^2 D, \\ \tau_{nm}^{-1} = \tau_n^{-1} + \tau_m^{-1} = (n^2 + m^2) D. \quad (5.2)$$

Thus  $g_{ij}^{(T)}(\tau)$  for  $i \neq j$  is now nonvanishing even though the motions of the two rotors are uncorrelated, a result which follows because the splittings are correlated through the spin-density fluctuations. Specific examples of the linewidth variations resulting from this model are discussed in Parts (ii) and (iii) below.

##### Case c. Locked Pair of Rotors Undergoing Free Rotational Diffusion as a Unit

Only the leading terms of the Fourier series, Eq. (3.3), are retained in order to minimize the complexity, and we write

$$a_i(t) = A_i + B_{i;n} \cos n\theta_1 + C_{i;n} \cos n\theta_2 + D_{i;nn} \cos n\theta_1 \cos n\theta_2, \quad (5.3)$$

where  $n=1$  if only odd harmonics are important [see parts (ii) and (iii) below] or  $n=2$  if only even harmonics are important. The average splitting is

$$\bar{a}_i = A_i + \frac{1}{2} D_{i;nn} \cos n\alpha_{12}, \quad (5.4)$$

where  $\alpha_{12} = \theta_1 - \theta_2$  is the fixed angle between the two rotors. Evaluation of the integrals for the correlation functions gives

$$g_{ij}^{(T)}(\tau) = (\gamma_e^2/2) \left\{ [(B_{i;n} B_{j;n} + C_{i;n} C_{j;n}) + (B_{i;n} C_{j;n} + C_{i;n} B_{j;n}) \cos n\alpha_{12}] \exp[-\tau/(2\tau_n)] + \frac{1}{2} D_{i;nn} D_{j;nn} \exp(-2\tau/\tau_n) \right\}, \quad (5.5)$$

where  $\tau_n$  is given by Eq. (5.2) and the factor of  $\frac{1}{2}$  enters the first exponential because the diffusing unit here consists of two rotors [ $D_T = \frac{1}{2}D$ , see Eq. (A21)]. If any additional terms appropriate for two rotors are included in the Fourier series than just those retained in Eq. (5.3), cross terms such as  $B_{i;n}D_{j;nm}$  enter into the correlation functions.

## ii. Splittings within the Rotating Groups

We consider radicals with two identical substituents such as the *p*-dinitrofluorene anion or *p*-dihydroxybenzene cation. The  $^{14}\text{N}$  splitting in a nitro or amino group, or the proton splitting in a hydroxy, amino, or formyl group, is governed only by even harmonics in the Fourier series, so the leading terms in the preceding equations are for  $n=2$ . By symmetry, we have  $B_{1;2} = C_{2;2}$ ,  $B_{2;2} = C_{1;2}$ , and  $D_{1;22} = D_{2;22}$ , and denoting these three different coefficients by  $B$ ,  $C$ , and  $D$ , respectively, the correlation functions for the uncorrelated freely diffusing rotors are, from Eq. (5.1),

$$g_{11}^{(j)}(\tau) = \gamma_e^2 \left[ \frac{1}{2}(B^2 + C^2) \exp(-\tau/\tau_2) + \frac{1}{4}D^2 \exp(-2\tau/\tau_2) \right], \quad (5.6a)$$

$$g_{12}^{(j)}(\tau) = \gamma_e^2 \left[ BC \exp(-\tau/\tau_2) + \frac{1}{4}D^2 \exp(-2\tau/\tau_2) \right]. \quad (5.6b)$$

The correlation functions, as well as the spectral densities, obey the relation  $|g_{12}^{(j)}(\tau)| \leq g_{11}^{(j)}(\tau)$ , and the condition on the spectral densities for a large alternating linewidth effect, namely,  $j_{12}^{(j)}(\omega) \cong -j_{11}^{(j)}(\omega)$ , is satisfied if  $B \cong -C$ , provided that  $D$  is not too large. On the other hand, if  $B = C$ ,  $j_{12}^{(j)}(\omega) = j_{11}^{(j)}(\omega)$ , and there is only a quadratic dependence of the linewidth on  $M$  [see Eq. (2.7)].

For two locked rotors, Eq. (5.5) gives

$$g_{ij}^{(j)}(\tau) = (\gamma_e^2/2) \left\{ [(B+C)^2 \cos^2 \alpha_{12} + (-1)^{i+j}(B-C)^2 \sin^2 \alpha_{12}] \exp(-\tau/(2\tau_2)) + \frac{1}{4}D^2 \exp(-2\tau/\tau_2) \right\} \quad (5.7)$$

for  $i=1, 2$  and  $j=1, 2$ . Again  $|g_{12}^{(j)}(\tau)| \leq g_{11}^{(j)}(\tau)$ . If  $\alpha_{12} = 0$  or  $\pi$ ,  $j_{12}^{(j)}(\omega) = j_{11}^{(j)}(\omega)$ , there is a quadratic dependence of the linewidth on  $M$ , and the linewidth variation is greatest when  $B=C$  while it is smallest when  $B=-C$ . If  $\alpha_{12} = (\pi/2)$ , and  $D$  is not too large,  $j_{12}^{(j)}(\omega) \cong -j_{11}^{(j)}(\omega)$ , and there is an alternating linewidth effect provided  $B \neq C$ ; the effect is largest when  $B = -C$ .

The present results reduce to those of Sec. IV for  $C_{i;n} = D_{i;nm} = 0$ , as they must, but now because of the nonvanishing values of these terms there is a coupling through the pi-electron spin-density distribution as well as through the motion, so that an alternating linewidth effect can result even if the motions of the two rotors are uncorrelated. Whether or not the motions are correlated, however, an alternating linewidth does not result unless  $B \cong -C$  and  $D$  is not too large.

The only theoretical estimates of the coefficients are for the nitrobenzenes, and molecular-orbital calculations<sup>34</sup> indicate that  $B$  and  $C$  should, in fact, have opposite signs. The predictions are thus in agreement with the observed alternating linewidth phenomenon found in the *p*-dinitrofluorene and *m*-dinitrobenzene anions.<sup>2,4,5</sup> Physically the result of the MO calculations can be understood by considering the dinitrobenzene anion to consist of two parts, a nitrobenzene fragment and a nitro-group fragment. The nitrobenzene fragment has a greater electron affinity than an isolated nitro group so that when a nitro group is rotated out of the plane of the ring the unpaired electron tends to be localized in the nitrobenzene fragment. As a result, when one nitro group in a dinitrobenzene anion is rotated out of the plane of the ring, its  $^{14}\text{N}$  splitting decreases, while if the second nitro group is also rotated out of the plane, the splitting of the first group increases. These results are to be contrasted to the behavior of a mononitrobenzene where, as shown by the work of Geske and co-workers<sup>30,31</sup> and also by the MO calculations,<sup>34</sup> rotation of the nitro group out of the plane of the ring increases the  $^{14}\text{N}$  splitting. It should be noted that the alternating linewidth variation found in the dihydroxyfluorene cation<sup>1</sup> arises from the ring protons, not the hydroxy protons (see below).

## iii. Ring and Methyl-Group Splittings

### (a) Ring Splittings in Derivatives of 1,4-dinitrobenzene

For the 1,4-dinitrobenzenes, the hyperfine splittings at the ring positions satisfy the relations

$$a_i(\theta_1, \theta_4) = a_i(\theta_1 + \pi, \theta_4) = a_i(\theta_1, \theta_4 + \pi) = a_i(\theta_1 + \pi, \theta_4 + \pi), \quad (5.8a)$$

$$a_2(\theta_1, \theta_4) = a_6(\theta_1, \theta_4); \quad a_3(\theta_1, \theta_4) = a_5(\theta_1, \theta_4), \quad (5.8b)$$

$$a_2(\theta_1, \theta_4) = a_3(\theta_4, \theta_1). \quad (5.8c)$$

Equations (5.8a) follow from the twofold symmetry of the nitro groups, and Eqs. (5.8b) from the twofold symmetry of the rest of the molecule (excluding the nitro groups) for arbitrary orientations of the nitro groups. Similar nuclei at the four ring positions therefore form an equivalent group, and those at Positions 2 and 6 form one completely equivalent subgroup while nuclei at Positions 3 and 5 form another. The coefficients in the Fourier series, which involve only even harmonics, are consequently the same for Positions 2 and 6, and for Positions 3 and 5, but those for Positions 2 and 3 are different. For the leading terms, letting  $A = A_2$ ,  $B = B_{2;2}$ ,  $C = C_{2;2}$ , and  $D = D_{2;22}$ , we find, on using Eqs. (5.8), that  $A_3 = A$ ,  $B_{3;2} = C$ ,  $C_{3;2} = B$ , and  $D_{3;22} = D$ . Thus if we denote the completely equivalent subgroup containing nuclei at Positions 2 and 6 by 1, and the group containing nuclei at Positions 3 and 5 by 2, Eqs. (5.6) and (5.7) give the required correlation

functions. The secular contributions to the linewidth for this model, as calculated from Eq. (2.7), are presented in Table I for the *p*-dinitrobenzene and dinitro-durene anions, assuming for the latter compound that the methyl-group proton splittings are proportional to the pi-electron spin density on the adjacent ring carbon atoms. When  $j_{12}^{(T)}(0) = -j_{11}^{(T)}(0)$ , and  $j_{11}^{(T)}(0)$  is large (so that the modulation of the isotropic interaction makes a significant contribution to the linewidth), only the narrowest component of a hyperfine line is observed in the spectrum, and the lines alternate in width from sharp [width contribution: 0] to broad [width contribution:  $j_{11}^{(T)}(0)$ ], as discussed in Sec. II.

(b) *Ring Splittings in Derivatives of 1,4-dihydroxybenzene*

The symmetry relations obeyed by the hyperfine splittings at the different ring positions of the 1,4-dihydroxybenzenes are

$$a_2(\theta_1, \theta_4) = a_6(\theta_1 + \pi, \theta_4 + \pi); \quad a_3(\theta_1, \theta_4) = a_5(\theta_1 + \pi, \theta_4 + \pi) \quad (5.9)$$

and also Eq. (5.8c). We note that Eqs. (5.8b) follow from Eqs. (5.9) if Eqs. (5.8a) hold, but that Eq. (5.8a) does not apply to hydroxyl groups. We shall thus assume that the leading terms in the Fourier series are functions of the first harmonic of the orientations of the two rotors, i.e.,  $n=1$ . Similar nuclei at the four positions are equivalent, but not completely equivalent. Letting  $A = A_2$ ,  $B = B_{2,1}$ ,  $C = C_{2,1}$ , and  $D = D_{2,11}$ , we find on using these symmetry relations and examining the leading terms in the Fourier series, that  $A_i = A$ ,  $D_{i,11} = D$ ,  $B_{3,1} = -B_{6,1} = -C_{6,1} = C$ , and  $C_{3,1} = -C_{6,1} = -B_{6,1} = B$ . For the uncorrelated free-rotational diffusion model, let

$$\begin{aligned} g_C(\tau) &= (\gamma_e^2/4)(B+C)^2 \exp(-\tau/\tau_1), \\ g_T(\tau) &= (\gamma_e^2/4)(B-C)^2 \exp(-\tau/\tau_1), \\ g_{CT}(\tau) &= (\gamma_e^2/4)D^2 \exp(-2\tau/\tau_1), \end{aligned} \quad (5.10)$$

and for the rotational diffusion of two locked rotors, let

$$\begin{aligned} g_C(\tau) &= (\gamma_e^2/2)(B+C)^2 \cos^2(\alpha_{12}/2) \exp(-\tau/2\tau_1) \\ g_T(\tau) &= (\gamma_e^2/2)(B-C)^2 \sin^2(\alpha_{12}/2) \exp[-\tau/(2\tau_1)] \\ g_{CT}(\tau) &= (\gamma_e^2/8)D^2 \exp(-2\tau/\tau_1). \end{aligned} \quad (5.11)$$

Then, for both models, the correlation functions satisfy the relations

$$\begin{aligned} g_{22}^{(T)}(\tau) &= g_C(\tau) + g_T(\tau) + g_{CT}(\tau), \\ g_{23}^{(T)}(\tau) &= g_{56}^{(T)}(\tau) = g_C(\tau) - g_T(\tau) + g_{CT}(\tau), \\ g_{25}^{(T)}(\tau) &= g_{36}^{(T)}(\tau) = -g_C(\tau) + g_T(\tau) + g_{CT}(\tau), \\ g_{26}^{(T)}(\tau) &= g_{35}^{(T)}(\tau) = -g_C(\tau) - g_T(\tau) + g_{CT}(\tau), \end{aligned} \quad (5.12)$$

with  $g_{ii}^{(T)}(\tau) = g_{22}^{(T)}(\tau)$  and  $g_{ij}^{(T)}(\tau) = g_{ji}^{(T)}(\tau)$ ,  $i$  (or  $j$ ) = 2, 3, 5, 6.

Comparison of these models with the four-jump *cis-trans* model treated in I, Sec. VI, shows that the relations between the correlation functions, Eqs. (5.12), are identical to Eqs. (I.6.8), and thus the secular contributions to the linewidths are given by Table IV of I. If  $D$  is not too large, and if  $j_C(0)$  or  $j_T(0)$ , or both, are appreciable in magnitude, an alternating linewidth is obtained. This result is independent of any relation between  $B$  and  $C$  or, in the locked-rotor model, of the angle  $\alpha_{12}$  between the two rotors. In the *p*-dihydroxybenzenes, in contrast to the other examples treated, there is an out-of-phase correlation of the hyperfine splittings at the different ring positions that is determined by the symmetry of the problem so that the alternation in linewidth results directly from the symmetry. In the other cases considered, the out-of-phase correlation had to be introduced by a condition that was not required by symmetry. Thus the hyperfine splittings had to be related to the motion in some specific manner (such as the relation  $B = -C$  in the previous examples of this section), and/or the motions of the two rotors had to be coupled.

The essential difference between the *p*-dihydroxy- and *p*-dinitrobenzenes arises from the inclusion, because of the symmetry of the groups, of the odd harmonics in the Fourier series for the former. The even harmonics (those for which  $B_{i;2n+1} = C_{i;2n+1} = D_{i;2n+1,m} = D_{i;n,2m+1} = 0$ ), satisfy the conditions of Eq. (5.8a). The remaining terms, the odd harmonics (those for which  $B_{i;2n} = C_{i;2n} = D_{i;2n,2m} = D_{i;2n+1,2m+1} = 0$ ) satisfy the condition

$$a_i(\theta_1, \theta_4) - A_i = -[a_i(\theta_1 + \pi, \theta_4 + \pi) - A_i]. \quad (5.13)$$

Since the splittings satisfy Eqs. (5.8c) and (5.9), it follows from Eq. (5.8a) that for the even harmonics  $g_{22}^{(T)}(\tau) = g_{26}^{(T)}(\tau) = g_{35}^{(T)}(\tau)$  and  $g_{23}^{(T)}(\tau) = g_{25}^{(T)}(\tau) = g_{36}^{(T)}(\tau) = g_{56}^{(T)}(\tau)$ . Similarly, but with Eq. (5.13) instead of Eq. (5.8a), the odd harmonics give  $g_{22}^{(T)}(\tau) = -g_{26}^{(T)}(\tau) = -g_{35}^{(T)}(\tau)$  and  $g_{23}^{(T)}(\tau) = g_{56}^{(T)}(\tau) = -g_{25}^{(T)}(\tau) = -g_{36}^{(T)}(\tau)$ . Thus all of the odd harmonics automatically give an alternating linewidth, but the even harmonics produce a linewidth alternation only if special relations exist among the terms in the Fourier series or in the relative motions of the two rotors, and some of the even harmonics always give a quadratic dependence on  $M$  rather than an alternation in width (e.g., the  $D_{i,11}$  term).

## VI. DISCRETE JUMP MODELS

As indicated in Sec. III, internal rotations can be described under certain restrictive assumptions in terms of a discrete jump model<sup>15</sup> rather than as a Bownian-motion diffusion, and in this section we indicate how the rotations of groups with one- and twofold symmetry (such as hydroxyl and nitro groups) can be approximated in this way. Since the same mathematical treatment is also applicable to the description of switching motions in which an atom or group jumps

from one site in the radical to another, these are also briefly considered.

### i. Rotations of Groups with Twofold Symmetry

Probably the most realistic way of handling the rotational motions of a group with twofold symmetry, such as a nitro group, in terms of a discrete jump model, is to assume that the only possible conformations are those in which the group is either coplanar or perpendicular to the plane of the aromatic system. A molecule with two such groups equivalently situated could then exist in four different instantaneous conformations, *A*, *B*, *C*, and *D*. State *A* is defined as the conformation in which Group 1 is in the coplanar orientation and Group 2 in the perpendicular orientation, and in state *C* the orientations of the two groups are interchanged. These two states are thus thermodynamically equivalent. In State *B*, both groups are in the perpendicular orientation and in State *D*, both are coplanar. The interconversion of the different states is assumed to be governed by the equations



and two additional equations similar to Eqs. (6.1a) and (6.1b) with *A* replaced by *C*. Since these six rate equations involve seven different (and in general unknown) rate constants, their solution is very unwieldy, and we therefore treat only some special cases. By neglecting State *D*, the four-jump model can be reduced to a three-jump problem that is easily solved, and the detailed results are given in Appendix B. Neglecting State *D* is equivalent to assuming that the conformation in which both groups are simultaneously coplanar is of low probability. Since the completely coplanar state of dinitrobenzene is highly hindered, the three-jump model is not too unrealistic a representation of this molecule. A still more restricted aspect of the model is obtained by also neglecting State *B*. In the resulting two-jump model, one group is in a coplanar conformation while the other is simultaneously perpendicular, and the difference between the two states (*A* and *C*) just involves the switching of the roles of the two groups. The two-jump model has also been treated in Sec. V of I.

As an example of the application of the three-jump model, we consider a dinitrobenzene anion. The  $^{14}\text{N}$

splittings satisfy the relations

$$\begin{aligned} a_1(A) &= a_2(C) = a_I, \\ a_2(A) &= a_1(C) = a_{II}, \\ a_1(B) &= a_2(B) = a_{III}, \end{aligned} \quad (6.2)$$

where  $a_i(\mu)$  is the splitting from the  $i$ th nucleus in the  $\mu$ th state. The splittings  $a_I$  and  $a_{II}$  are for the in-plane and perpendicular nitro groups, respectively, in a molecule with one coplanar and one perpendicular nitro group, while  $a_{III}$  is the  $^{14}\text{N}$  splitting in a molecule in which both groups are perpendicular. Equations (6.2) also apply to the ring-proton splittings in the *p*-dinitrobenzene anion or the methyl-proton splittings in the dinitrobenzene anion if the subscripts 1 and 2 refer to the two different completely equivalent subgroups with the nuclei at Positions 2 and 6 being in Group 1 and those at Positions 3 and 5 in Group 2, as in Sec. V.iii.a above. The average hyperfine splitting is

$$\bar{a} = \bar{a}_1 = \bar{a}_2 = W(A)[a_I + a_{II} - 2a_{III}] + a_{III}, \quad (6.3)$$

where  $W(A)$  is the probability of finding the system in the state *A*, and  $W(A) = W(C)$  with  $W(B) = 1 - 2W(A)$ . By using the conditional probabilities in Appendix B and the relations in Eqs. (6.2), it is readily shown that the correlation functions are

$$\begin{aligned} g_{ij}^{(T)}(\tau) &= (\gamma_e^2/2)W(A)\{(-1)^{i+j}(a_I - a_{II})^2 \exp(-\tau/\tau_1) \\ &\quad + W(B)(a_I + a_{II} - 2a_{III})^2 \exp(-\tau/\tau_2)\}, \end{aligned} \quad (6.4)$$

where the correlation times  $\tau_1$  and  $\tau_2$  are given by

$$\tau_1^{-1} = k_1 + 2k_3, \quad \tau_2^{-1} = k_1 + 2k_1'. \quad (6.5)$$

If the probability  $W(B)$  of the conformation in which both groups are simultaneously in the perpendicular orientation is negligible, corresponding to the two-jump model treated in I, the term in  $\tau_2$  in Eq. (6.4) vanishes and  $j_{12}^{(T)}(\omega) = -j_{11}^{(T)}(\omega)$ . Thus when  $W(B) = 0$ , there is an alternation in the linewidths, but if  $W(B) \neq 0$ ,  $|j_{12}^{(T)}(\omega)| \leq j_{11}^{(T)}(\omega)$  so that a nonnegligible probability of the occurrence of State *B* can cause a reduction in the extent of the alternating linewidth effect. If the splitting from the  $^{14}\text{N}$  nucleus in Group 1 depends only on the orientation of Group 1,  $a_{III} = a_{II}$ . This corresponds to the assumptions of Sec. IV in which the spin-density modulations were omitted.

It is also possible to treat simply a somewhat less realistic model. Instead of neglecting the state in which both nitro groups are simultaneously coplanar, we assume that it has the same probability as the conformation in which both groups are perpendicular, i.e.,  $W(B) = W(D)$  and  $k_1 = k_2$ ,  $k_1' = k_2'$ ,  $k_4' = k_4$ . This problem is analyzed in Sec. VI of I, and the correlation functions are given by Eq. (I.6.6).

### ii. Rotations of Hydroxyl and other Similar Groups

An analogous treatment of the conformation of a single group like  $-\text{OH}$  that does not possess twofold

symmetry requires four instantaneous orientations because the two coplanar states as well as the two perpendicular states are different. A molecule with two hydroxyl groups would thus be represented by 16 states. The spin-density distribution in radicals like the *p*-dihydroxybenzene or dihydroxydurene cations are identical in the four states with all the hydroxyl groups in the perpendicular orientation, but the spin densities in each of the four coplanar states can all be different. We have not attempted to solve the general 16-jump problem, but the four-jump model consisting of only the coplanar conformations is readily solved and leads to linewidth variations for the lines from ring-position splittings (either ring protons or methyl-group protons). The detailed analysis of this problem is given in Sec. VI of I.

The hydroxyl-proton splittings in all of the allowed conformations of this four-jump coplanar model are identical, and thus no linewidth variations are predicted for the lines from these splittings. To illustrate how linewidth effects can arise for the hydroxyl-proton lines, we treat a tractable but unrealistic model: It is assumed that whenever Group 1 is in one of the two coplanar orientations, Group 2 is always in one of the two perpendicular orientations, and vice versa. In this way the 16-jump problem is reduced to a four-jump problem in which there is only one thermodynamically distinct conformation, and again the analysis of Sec. VI of I is applicable. If  $a_I$  is the hydroxyl-proton splitting for the hydroxyl group that is in the plane of the ring, and  $a_{II}$  the splitting for the group that is perpendicular, one finds from I that the correlation function is

$$g_{11}^{(D)}(\tau) = -g_{12}^{(D)}(\tau) = (\gamma_e^2/4) [a_I - a_{II}]^2 \exp(-\tau/\tau_0), \quad (6.6)$$

where  $\tau_0 = \tau_{CT} = \tau_C = \tau_T$ .

### iii. Nonrotational Jump Models

Jump models provide a realistic description of molecular rearrangements such as those observed by de Boer and Mackor<sup>7</sup> in the pyracene anion and by Bolton and Carrington<sup>8</sup> in the naphthazarin cation. The first was treated as a two-jump problem and the second by a four-jump mechanism.<sup>13</sup> Fluctuations caused by solvent complexes can also sometimes be analyzed by jump models.<sup>14</sup> Equations (6.1), for example, can represent solvation complexes in compounds like the dinitrobenzenes or benzosemiquinones as well as other radicals with two equivalent functional groups. In the dinitrobenzenes, State *A* could represent a complex between the solvent and one nitro group and State *C* a complex with the other nitro group. State *B* could then be the uncomplexed species and State *D* the doubly complexed radical. The details of the analysis are identical to those of the preceding parts of this section. The electron transfer induced by solvent perturbations in dinitrophenyls can also be described by a jump process.<sup>8</sup>

## VII. SUMMARY AND CONCLUSIONS

These calculations show that the fluctuations in isotropic hyperfine splittings in free radicals caused by internal motions can produce pronounced effects in the appearance of the ESR spectra. The most spectacular manifestation, the alternation in widths from one hyperfine component to another, occurs when there is an out-of-phase correlation between the hyperfine splittings of different nuclei. More precisely, if two nuclei *i* and *j* are equivalent, so that their average hyperfine splittings are equal ( $\bar{a}_i = \bar{a}_j$ ), the maximum alternating linewidth effect arises when the spectral densities satisfy the relation  $j_{ij}^{(D)}(\omega) = -j_{ii}^{(D)}(\omega)$ . This condition results if the instantaneous hyperfine splittings  $a_i(t)$  and  $a_j(t)$  are correlated in such a way that  $a_i(t)$  reaches a maximum while  $a_j(t)$  is at a minimum, and vice versa. On the other hand, if  $a_i(t) = a_j(t)$ , nuclei *i* and *j* are completely equivalent,  $j_{ij}^{(D)}(\omega) = j_{ii}^{(D)}(\omega)$ , and these linewidth anomalies do not occur. Intermediate cases in which there is only partial out-of-phase correlation give spectral densities that are related by  $-j_{ij}^{(D)}(\omega) \lesssim j_{ii}^{(D)}(\omega)$ . An alternation in linewidths may also result under these circumstances, but it is not as pronounced as when  $j_{ij}^{(D)}(\omega) = -j_{ii}^{(D)}(\omega)$ . Similar effects occur for sets of nuclei that can be subdivided into completely equivalent subgroups. More complicated patterns may ensue when the hyperfine splittings from more than two different completely equivalent subgroups are correlated. Thus the rotations of several methyl groups are predicted to cause spectra in which every third line is narrow and the remaining lines broad.<sup>19</sup>

The out-of-phase correlation which produces the alternating linewidth effect can result from internal molecular rotations whenever the hyperfine splittings vary with the rotations and are correlated with the proper relative phases. The correlation may be caused by a coupling of the mechanical motions of different rotating groups, but even if the motions of different groups are independent, the correlation of splittings may result from the dependence of the spin-density distribution on orientation. In radicals such as the dihydroxybenzene cation a partial out-of-phase correlation is brought about directly by the symmetry, while in radicals like the *p*-dinitrobenzene anion the nature of the correlation depends on the form of both the dynamical motions and the spin-density variations. Fluctuating solvent complexes can cause effects that are similar to internal rotating motions. A number of different models for the motions and spin-density variations can be formulated so as to yield an out-of-phase correlation of the hyperfine splittings. Continuous motion cases treated by Brownian-motion theory give the same general features as the restricted-motion discrete jump models, thus demonstrating that it is usually impossible to establish uniquely the details of the motion from the merely qualitative observation of an alternating linewidth effect.

APPENDIX A.  
BROWNIAN MOTION DISTRIBUTION FUNCTIONS

In this Appendix, we summarize those results from the theory of Brownian motion that are needed to obtain the correlation functions and spectral densities which determine the relaxation matrix for free radicals containing rotating groups. A rotor is characterized by its moment of inertia  $I$  and friction constant  $\beta I$ . If the shape of the rotor approximates that of a (macroscopic) sphere, the quantity  $\beta$  is given by<sup>37</sup>  $\beta = 8\pi\eta a^3/I$ , where  $a$  is the radius of the sphere and  $\eta$  the viscosity of the fluid. It is assumed that the Brownian motion is described by the Langevin equation in the angle of rotation  $\theta$ :

$$d^2\theta/dt^2 + \beta\theta = A(t) + f(\theta), \quad (\text{A1})$$

where  $A(t)$  is a random rotational acceleration<sup>35</sup> which describes the torques resulting from solvent collisions and  $f(\theta)I$  is the external torque applied to the rotor. For a single rotor undergoing free rotational diffusion,  $f(\theta) = 0$ , while for a rotor subject to a harmonic restoring force,  $f(\theta) = -\omega_0^2(\theta - \theta_e)$  where  $\omega_0/2\pi$  is the frequency of the oscillation,  $\theta_e$  is the equilibrium position, and the displacements,  $y = \theta - \theta_e$ , are assumed to be small.

For free rotational diffusion, the probability of finding the rotor at any angle  $\theta_0$ ,  $0 \leq \theta_0 \leq 2\pi$ , is independent of  $\theta_0$  and is given by

$$W(\theta_0)d\theta_0 = (1/2\pi)d\theta_0, \quad (\text{A2})$$

while the conditional probability [Eq. (I.2.4 ff)] that the rotor is at the angle  $\theta$  at the time  $\tau \geq 0$  if it was at  $\theta_0$  at time  $\tau = 0$  is<sup>35</sup>

$$P(\theta_0 | \theta, \tau)d\theta = (4\pi D\tau)^{-1/2} \exp[-(\theta - \theta_0)^2/4D\tau]d\theta. \quad (\text{A3})$$

This equation holds for long times, i.e.,  $\tau \gg \beta^{-1}$ , and the diffusion constant  $D$  is given in terms of the friction constant by the Einstein relation

$$D = kT/(\beta I), \quad (\text{A4})$$

where  $k$  is the Boltzmann constant and  $T$  the absolute temperature. The angle  $\theta$  in Eq. (A3) may be anywhere in the range  $-\infty \leq \theta - \theta_0 \leq \infty$  since the rotor can make many complete revolutions during the time  $\tau$ .

For an harmonic oscillator the distribution in the displacement  $y_0 = \theta_0 - \theta_e$  from the equilibrium position is<sup>35</sup>

$$W(y_0)dy_0 = (\omega_0^2/2\pi\beta D)^{1/2} \exp[-(\omega_0^2 y_0^2/2\beta D)]dy_0. \quad (\text{A5})$$

Since  $(\omega_0^2/2\beta D) = (I\omega_0^2/2kI)$ , Eq. (A5) is the Boltzmann distribution in  $y_0$ . It follows immediately that  $\langle y_0 \rangle_{Av} = 0$  and

$$\langle y_0^2 \rangle_{Av} = (\beta D/\omega_0^2) = (kT/I\omega_0^2). \quad (\text{A6})$$

The normalization has been carried out on the assumption

<sup>37</sup> H. Lamb, *Hydrodynamics* (Cambridge University Press, Cambridge, 1932), p. 589. P. Debye, *Polar Molecules* (Dover Publications, Inc., New York, 1954).

tion that the displacements are small enough so that the interval  $(0, 2\pi)$  for  $y_0$  can be replaced by the interval  $(-\infty, \infty)$  without appreciable error. For the overdamped oscillator, corresponding to  $\beta \gg 2\omega_0$ , and for long times,  $\tau \gg \beta^{-1}$ , the conditional probability<sup>35b, 35c</sup> is

$$P(y_0 | y, \tau)dy = \left(\frac{\omega_0^2}{2\pi\beta D}\right)^{1/2} (1-\rho^2)^{-1/2} \times \exp\left[-\frac{\omega_0^2}{2\beta D} \frac{(y - \rho y_0)^2}{(1-\rho^2)}\right] dy. \quad (\text{A7})$$

Here

$$\rho = \rho(\tau) = [g^{(0)}(\tau)/\langle y^2 \rangle] = \exp[-(\omega_0^2/\beta)\tau],$$

where by definition (for any values of  $\beta$ ,  $\omega_0$ , and  $\tau$ )

$$g^{(0)}(\tau) = \langle y(t)y(t+\tau) \rangle = \langle [\theta(t) - \theta_e][\theta(t+\tau) - \theta_e] \rangle \quad (\text{A8})$$

is the correlation function [Eqs. (2.6) of I and Eq. (2.1) above].

If the oscillator is not overdamped, the conditional probability is a quite complicated function,<sup>35</sup> but it is possible to obtain the needed spectral densities directly without proceeding from the correlation functions. Defining the spectral density  $j^{(0)}(\omega)$  as one-half the Fourier transform of the correlation function  $g^{(0)}(\tau)$  [Eq. (2.2)], the method of Rice<sup>35c, 35d</sup> leads immediately from the Langevin equation to

$$j^{(0)}(\omega) = \beta^2 D [(\omega^2 - \omega_0^2)^2 + \beta^2 \omega^2]^{-1}. \quad (\text{A9})$$

We also require the correlation function

$$g^{(2)}(\tau) = \langle [y^2(t) - \langle y^2 \rangle_{Av}][y^2(t+\tau) - \langle y^2 \rangle_{Av}] \rangle \quad (\text{A10})$$

and its spectral density  $j^{(2)}(\omega)$ . Since the probability distribution  $W(\theta_0; \theta\tau)$  for the Brownian motion of a harmonic oscillator is still a two-dimensional Gaussian distribution for the general case,<sup>35e</sup> one can readily show that

$$g^{(2)}(\tau) = 2[g^{(0)}(\tau)]^2, \quad (\text{A11})$$

from which it follows that<sup>38</sup>

$$j^{(2)}(\omega) = \frac{2}{\pi} \int_{-\infty}^{\infty} j^{(0)}(\omega') j^{(0)}(\omega - \omega') d\omega'. \quad (\text{A12})$$

Evaluation of the integral gives

$$j^{(2)}(\omega) = \frac{4\beta^2 D^2 [16s^2(\omega_0^2 + \beta^2) - \omega^2(5\beta^2 + \omega^2)]}{\omega_0^2(\beta^2 + \omega^2)(4s^2 - \omega^2)[16\omega_0^4 + \omega^2(\omega^2 - 8\omega_0^2 + 4\beta^2)]}, \quad (\text{A13})$$

where

$$s = [\omega_0^2 - (\beta^2/4)]^{1/2}. \quad (\text{A14})$$

For  $\omega = 0$ , the spectral densities reduce to the simpler

<sup>38</sup> Reference 21, pp. 473 ff.

expressions

$$j^{(0)}(0) = \beta^2 D / \omega_0^4 \quad (\text{A15})$$

$$j^{(2)}(0) = (\beta D^2 / \omega_0^6) (\omega_0^2 + \beta^2) \\ = (D/\beta) [(\omega_0^2 + \beta^2) / \omega_0^2] j^{(0)}(0) \quad (\text{A16})$$

while for large damping ( $\beta \gg \omega_0$ ) and long times ( $\tau \gg \beta^{-1}$ ) in  $g(\tau)$ , corresponding to low frequencies ( $\omega \ll \omega_0$ ) in its Fourier transform  $j(\omega)$ ,

$$j^{(0)}(\omega) = (\beta D / \omega_0^2) \tau_1 (1 + \omega^2 \tau_1^2)^{-1}, \quad (\text{A17})$$

$$j^{(2)}(\omega) = (2\beta^2 D^2 / \omega_0^4) \tau_2 (1 + \omega^2 \tau_2^2)^{-1}, \quad (\text{A18})$$

where

$$\tau_1 = 2\tau_2 = (\beta / \omega_0^2). \quad (\text{A19})$$

For a radical containing several rotating groups, the cases considered in the text are those for which the angular displacements of the  $i$ th and  $j$ th rotors,  $\theta_i$  and  $\theta_j$ , are: (1) uncorrelated; (2) locked together at a fixed angle,

$$\alpha_{ij} = \theta_i - \theta_j; \quad (\text{A20})$$

and (3) oscillating about an equilibrium angle of separation. For  $N$  identical locked rotors [Case (2)], the above equations hold with the diffusion constant  $D$  replaced by

$$D_T = (1/N)D. \quad (\text{A21})$$

The Langevin equations for two identical rotors oscillating with respect to each other, and with each rotor oscillating about its own equilibrium position  $\theta_{ie}$ , are, in terms of the displacements  $y_i = \theta_i - \theta_{ie}$ ,

$$\frac{d^2 y_i}{dt^2} + \beta \frac{dy_i}{dt} + \omega_0^2 y_i \pm \omega_{12}^2 (y_1 - y_2 - \alpha_e) = A_i(t), \quad (\text{A22})$$

where the upper sign holds for  $i=1$  and the lower sign for  $i=2$ ,  $\omega_{12}^2$  is the angular frequency of the mutual attraction, and  $\alpha_e$  is the equilibrium separation. By transforming to the variables  $u_1$  and  $u_2$ ,

$$u_1 = \frac{1}{2}(y_1 + y_2), \quad (\text{A23a})$$

$$u_2 = \frac{1}{2}(y_1 - y_2 - r\alpha_e),$$

where

$$r = (2\omega_{12}^2) / (\omega_0^2 + 2\omega_{12}^2), \quad (\text{A23b})$$

one obtains

$$\frac{d^2 u_i}{dt^2} + \beta \frac{du_i}{dt} + \omega_i^2 u_i = B_i(t), \quad (\text{A24})$$

where

$$B_1(t) = \frac{1}{2}[A_1(t) + A_2(t)],$$

$$B_2(t) = \frac{1}{2}[A_1(t) - A_2(t)],$$

and

$$\omega_1^2 = \omega_0^2,$$

$$\omega_2^2 = \omega_0^2 + 2\omega_{12}^2. \quad (\text{A25})$$

We assume that the random forces which determine

$A_1(t)$  and  $A_2(t)$  are uncorrelated so that<sup>35c</sup>

$$\langle A_i(t) A_j(t+\tau) \rangle = 2\beta^2 D \delta(\tau) \delta_{ij}, \quad (\text{A26})$$

from which one obtains

$$\langle B_i(t) B_j(t+\tau) \rangle = \beta^2 D \delta(\tau). \quad (\text{A27})$$

The probability distributions in  $u_1$  and  $u_2$  are thus identical to those above for a single oscillating rotor [Eqs. (A5) to (A19)] with Eqs. (A25) for the angular frequencies and with  $D_T = \frac{1}{2}D$  for the diffusion constant. If the coupled rotors are allowed to rotate freely as a group, the solutions are obtained by setting  $\omega_0 = 0$ , and the probability distributions in  $u_1$  are given by the expressions in Eqs. (A2) and (A3) with  $D$  replaced by  $D_T$ . For this case, the displacement variables  $y_i$  become identical to  $\theta_i$ , and  $r = 1$ .

### APPENDIX B. THREE-JUMP MODEL

We assume that the system can exist in three states,  $A$ ,  $B$ , and  $C$ , and that States  $A$  and  $C$  are thermodynamically equivalent. The three states are interrelated by the rate equations of Sec. VI, Eqs. (6.1). The probabilities of occurrence of the states are

$$W(A) = W(C) = k_1' / (k_1 + 2k_1'),$$

$$W(B) = [1 - 2W(A)] = k_1 / (k_1 + 2k_1'). \quad (\text{B1})$$

The conditional probabilities  $P(A | \mu, \tau)$  of finding the system in state  $\mu$  at the time  $\tau \geq 0$  when it was in state  $A$  at time  $\tau = 0$  are readily found to be

$$P(A | A, \tau) = W(A) + \frac{1}{2} \exp(-\tau/\tau_1) \\ + \frac{1}{2} W(B) \exp(-\tau/\tau_2)$$

$$P(A | B, \tau) = W(B) [1 - \exp(-\tau/\tau_2)]$$

$$P(A | C, \tau) = W(A) - \frac{1}{2} \exp(-\tau/\tau_1) \\ + \frac{1}{2} W(B) \exp(-\tau/\tau_2), \quad (\text{B2})$$

where  $\tau_1$  and  $\tau_2$  are given by Eqs. (6.5). Similar expressions with  $A$  and  $C$  interchanged hold when the system is initially in State  $C$ . When the system is initially in State  $B$

$$P(B | A, \tau) = P(B | C, \tau) = W(A) [1 - \exp(-\tau/\tau_2)]$$

$$P(B | B, \tau) = W(B) + 2W(A) \exp(-\tau/\tau_2). \quad (\text{B3})$$

The average hyperfine splitting is

$$\bar{a}_i = W(A) [a_i(A) + a_i(C)] + W(B) a_i(B), \quad (\text{B4})$$

and the correlation functions are readily found to be given by

$$g_{ij}^{(X)}(\tau) = (\gamma_i^2/2) \{ W(A) \exp(-\tau/\tau_1) \\ \times [a_i(A) - a_i(C)] [a_j(A) - a_j(C)] \\ + W(A) W(B) \exp(-\tau/\tau_2) [a_i(A) + a_i(C) - 2a_i(B)] \\ \times [a_j(A) + a_j(C) - 2a_j(B)] \}. \quad (\text{B5})$$