Angular dependence of the β-proton isotropic hyperfine coupling constant

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(Received 20 December 1971)

The angular dependence of the β-proton isotropic hyperfine coupling in alkyl or π radicals is investigated using a limited CI approach. Values of B_0 and B_2 for the equation $A_\beta = B_0 + B_2 \cos^2\theta$ are found to be 2.71 and 50.14 G, respectively. The dominant contribution is found to arise from an electron exchange mechanism. Approximate treatment of this term by a simple charge transfer model leads to an expression for the β-proton coupling constant, $A_\beta = 413.2\{1 + \text{sgn}F(\theta)[1 + F(\theta)^{-2}]^{-1/2}\}$, where $F(\theta)$ is a simple function of the angular variable $\cos\theta$ and $\text{sgn}F(\theta)$ indicates its sign. The CI study also shows that the $\cos^4\theta$ factor in a power series expansion of A_β makes a negligible contribution to the hyperfine coupling.

I. INTRODUCTION

For β protons in alkyl or π radicals, the relationship between the hyperfine coupling $A_H(\theta)$ and the spin density ρ has been given by the relation

$$A_H(\theta) = Q_\beta(\theta)\rho, \qquad (1)$$

where $Q_\beta(\theta)$ has been expressed in the form[1]

$$Q_\beta(\theta) = B_0 + B_2 \cos^2\theta. \qquad (2)$$

In Eq. (2), θ is the angle shown in Fig. 1, and B_0 and B_2 are constants.

Whiffen[2] has pointed out that the empirical expression for $Q_\beta(\theta)$ will change if molecular motion occurs. Torsional oscillations will give rise to temperature-dependent couplings which will vary between the limits of a frozen configuration with discrete values of θ, to a freely rotating methyl group with a time-averaged value of θ. This paper is concerned with methyl groups in a frozen configuration, or with species such as the methylene groups which cannot rotate because of geometric factors as, for example, in cyclic radical systems. Zero-point oscillations in such molecules are expected to be small and independent of the particular radical involved.

There is not complete agreement on the values which should be assigned to B_0 and B_2 in Eq. (2). Horsfield, Morton, and Whiffen[3] have calculated values of B_0 and B_2 which fit the hyperfine couplings for $CH_3\dot{C}HCO_2^-$ trapped in α-alanine at 77°K. These authors give $B_0 = 3.60$ G and $B_2 = 51.46$ G.[4] With the possible exception of the radical $CH_3CH_2\dot{C}(CO_2H)_2$, numerous B_2 values between 38 and 54 G have been recorded for other radicals.[5] There also appears to be some disagreement as to the sign of the B_0 term. The calculations of Colpa and de Boer[6] lead to a negative sign for B_0. This value is the sum of a direct spin polarization term, a negative contribution, and an indirect through-bond spin polarization which is a positive contribution. A positive value of B_0 has been used to fit Eq. (2) to experimental results for radicals exhibiting torsional motion.[2]

Disagreement as to the actual mechanism leading to the observed isotropic coupling is also found. While Colpa and de Boer's calculations for in-plane protons suggest that induced spin polarization is only a rather small contribution to the total hyperfine coupling, Luz[7] has found that through-bond spin polarization provides a much larger contribution for out-of-plane protons, being approximately 50% of the observed coupling. For this latter result to be correct, spin polarization effects of necessity must change markedly with variation of θ, a fact which is not entirely in keeping with expectations based on earlier calculations.[8] Karplus and Lazdins[9a] have carried out semiempirical calculations on β-coupling constants for the freely rotating ethyl radical but did not consider the θ angular dependence explicitly. They found that charge transfer mechanisms, which were not considered in the two calculations mentioned above, contributed nearly 40% to the total hyperfine coupling.

We have therefore undertaken to determine the dominant mechanism producing the isotropic coupling of static β protons using nonempirical techniques. More particularly, however, we wish to obtain a theoretical fit to Eq. (2) and to study the effect of adding terms such as $\cos^4\theta$ in an extended power series expansion of this equation. To this end, B_0, B_2, and B_4 are determined to different levels of approximation.

II. THEORY

At high magnetic fields the isotropic electron–nuclear spin interaction is adequately approximated by

$$H_F = (8\pi/3) g_e g_n \beta_e \beta_n \sum_k \delta(r_{kN}) S_{kz} I_{kz}, \qquad (3)$$

where the symbols have their usual meaning. The isotropic hyperfine interaction constant (in gauss) for the nucleus N is given by

$$A_N = \langle \Psi \mid H_F \mid \Psi \rangle \{g_e \beta_e \langle S_z \rangle \langle I_z \rangle\}^{-1}. \qquad (4)$$

In this expression Ψ is the total electronic wavefunction and $\langle S_z \rangle$ is the expectation value of the total spin of the radical ($\langle S_z \rangle = +\frac{1}{2}$). The wavefunction Ψ may be expanded in some basis set,

$$\Psi = \sum_i C_i \chi_i, \qquad (5)$$

which allows the hyperfine coupling constant to be expressed as

$$A_N = \sum_i \sum_j \langle \chi_i \mid H_F \mid \chi_j \rangle C_i C_j \{ g_e \beta_e \langle S_z \rangle \langle I_z \rangle \}^{-1}. \quad (6)$$

Since the β protons of paramagnetic species are of primary concern in systems of interest, Eq. (6) may be rewritten as

$$A_H = 507.1 \sum_i \sum_j \Omega_{ij} C_i C_j, \quad (7)$$

where

$$\Omega_{ij} = \rho_{ij}(r_H) \{ \mid 1s(0) \mid^2 \}^{-1} \quad (8)$$

and $\rho_{ij}(r_H)$ is the spin density at the proton, defined by

$$\rho_{ij}(r_H) = \langle \chi_i \mid \sum_k \sigma_{zk} \delta(r_{kH}) \mid \chi_j \rangle. \quad (9)$$

σ_{zk} is the Pauli spin operator and χ_i is one member of a basis set to be described shortly.

The calculations are performed by means of ASMO CI procedure. To implement this method in a non-empirical manner, the simplest possible fragment has been chosen, which is the system shown in Fig. 1. The effect of the sigma bond between the two carbon atoms is not considered, and the fragment therefore corresponds to the extended model of McConnell and Chesnut.[10] The interaction between the "unpaired electron contained in a π orbital" and the electrons of the C–H bond is calculated for different values of θ. This model represents a weakly bound C$\cdots$C–H system, and the interactions considered involve direct spin polarization and direct electron transfer. "Direct" in the context employed here refers to a "through-space" coupling. Some comments as to the indirect processes which have been neglected appear in the discussion section.

The basis set consists of the following orbitals:

$$\sigma_b = \{1s + te\} \{2(1+S)\}^{-1/2}, \quad (10)$$

$$\sigma_a = \{1s - te\} \{2(1-S)\}^{-1/2}, \quad (11)$$

where te is a hybrid-type orbital given by

$$te = \tfrac{1}{2} \{ (2s) + 3^{1/2}(2p) \}, \quad (12)$$

and S is the overlap integral $\langle 1s \mid te \rangle$. The third orbital employed is the π orbital "containing the unpaired electron." The direct contact contribution of spin density in the π orbital to the hyperfine coupling of a β proton is not large. Integrals of the form $\langle \pi \mid \sigma_{zk} \delta(r_{kH}) \mid \pi \rangle$ have been investigated using the carbon Hartree-Fock orbitals of Jucys,[11] and were found to be small enough to neglect to a fair degree of approximation even for the $\theta = 0$ configuration.

Clearly for the out-of-plane β protons, the σ and π orbitals are not orthogonal. As Melchior[12] has observed, the neglect of overlap in the computation of hyperfine coupling parameters has given rise to apparently erroneous conclusions concerning the importance of various factors contributing to the observed splittings. On the other hand, rigorous separation of hyperfine coupling
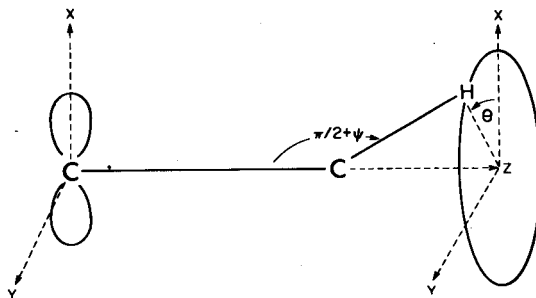

FIG. 1. Specification of the angles for the molecular fragment employed in the calculations.

into various mechanisms is not possible using an orthogonalized basis set. This is because there are a variety of equally valid orthogonalization procedures, each of which give different values for those various matrix elements which are taken to designate "spin polarization," "charge transfer," or their cross products. Since there is a very real reduction in the complexity of the θ angular dependence using an orthogonal basis set, we have followed this procedure in spite of the above difficulty, reasoning that in any case the deviation from orthogonality for the σ–π system represented by β-methyl protons is fairly small, and it is to be hoped that the results may therefore still be interpreted in terms of "spin polarization" and "charge transfer" as discussed by the authors cited above. There is no difficulty when one speaks of the total coupling constant since the calculated values of B_0 and B_2 will not depend on the particular method of orthogonalization. Accordingly we have chosen to work with the orthogonal set $[\Pi, \sigma_a, \sigma_b]$ where Π has been made orthogonal to the remaining orbitals by the Schmidt technique. Π then takes the form

$$\Pi = \{ \pi - S_{\pi b} \sigma_b - S_{\pi a} \sigma_a \} \{ 1 - S_{\pi b}{}^2 - S_{\pi a}{}^2 \}^{-1/2}, \quad (13)$$

where $S_{\pi b} = \langle \sigma_b \mid \pi \rangle$ and $S_{\pi a} = \langle \sigma_a \mid \pi \rangle$. Since this introduces $1s$ character into the Π orbital, matrix elements of the form $\langle \Pi \mid H_F \mid \Pi \rangle$ may no longer be neglected.

Six configurations have been included in the expansion given by Eq. (5). The approximate description of the ground state is represented by the normalized Slater determinant,

$$\chi_1 = \| \Pi \sigma_b \bar{\sigma}_b \|, \quad (14)$$

where the bar in Eq. (14) denotes spin β and no bar denotes spin α. Singly excited π–σ^* configurations can be described as

$$\chi_2 = 2^{-1/2} \{ \| \Pi \sigma_b \bar{\sigma}_a \| - \| \Pi \bar{\sigma}_b \sigma_a \| \}, \quad (15)$$

$$\chi_3 = 6^{-1/2} \{ 2 \| \bar{\Pi} \sigma_b \sigma_a \| - \| \Pi \bar{\sigma}_b \sigma_a \| - \| \Pi \sigma_b \bar{\sigma}_a \| \}, \quad (16)$$

based on the representation of the ground state χ_1 as given by Eq. (14). These configurations are eigenfunctions of $S_z(+\tfrac{1}{2})$ and $S^2(\tfrac{3}{4})$. They are responsible

TABLE I. Breakdown of the hyperfine coupling contributions when only nonpolar configurations are considered.

θ	i	j	Hyperfine factor Ω_{ij}[a]	C_i[b]	C_j	Contribution to hyperfine coupling constant (G)
0	1	1	0.3133×10^{-2}	0.9223	0.9223	1.3515
	1	2	0	0.9223	0.3864	0
	1	3	0.5664	0.9223	-0.4129×10^{-2}	-1.0939
	2	2	0.3133×10^{-2}	0.3864	0.3864	0.2372
	2	3	0.7704	0.3864	-0.4129×10^{-2}	-0.6233
	3	3	1.2823	-0.4129×10^{-2}	-0.4129×10^{-2}	0.0111
					Sum$=-1.83$	
45	1	1	0.1546×10^{-2}	0.9222	0.9222	0.6665
	1	2	0	0.9222	0.3868	0
	1	3	0.5664	0.9222	-0.1958×10^{-2}	-0.5186
	2	2	0.1546×10^{-2}	0.3868	0.3868	0.1173
	2	3	0.7704	0.3868	-0.1958×10^{-2}	-0.2959
	3	3	1.2828	-0.1958×10^{-2}	-0.1958×10^{-2}	0.0025
					Sum$=-0.84$	
90	1	1	0	0.9217	0.9217	0
	1	2	0	0.9217	0.3880	0
	1	3	0.5664	0.9217	0.3164×10^{-2}	0.8376
	2	2	0	0.3880	0.3880	0
	2	3	0.7704	0.3880	0.3164×10^{-2}	0.4796
	3	3	1.2833	0.3164×10^{-2}	0.3164×10^{-2}	0.0065
					Sum$=$ 2.64	

[a] See Eq. (8).

[b] These are coefficients given by Eq. (5).

for spin polarization effects, and do not involve charge migration.

Electron transfer from the center containing the π orbital gives an excited configuration χ_4,

$$\chi_4 = \| \sigma_a \sigma_b \bar{\sigma}_b \|, \tag{17}$$

while electron donation to the π center may be described by the configurations

$$\chi_5 = \| \Pi \sigma_b \bar{\Pi} \| \tag{18}$$

and

$$\chi_6 = \| \Pi \sigma_a \bar{\Pi} \|. \tag{19}$$

Doubly excited configurations such as $\| \Pi \sigma_a \bar{\sigma}_a \|$, $\| \sigma_a \sigma_b \bar{\sigma}_a \|$, etc., have been omitted.

The coefficients appearing in Eq. (5) are obtained by solution of the appropriate secular equation. The major difficulty occurs in the evaluation of the matrix elements $\langle \chi_i \mid H \mid \chi_j \rangle$ where H is the electronic Hamiltonian for the C$\cdots$C–H system. All necessary integrals were evaluated by the procedure of Huzinaga et al.[13] which employs a limited expansion in Gaussian-type functions for each Slater orbital. For $2s$ and $2p$ orbitals centered on the carbon atoms the orbital exponent was taken as $\zeta_C = 1.625$, while for the hydrogen $1s$ orbital, $\zeta_H = 1.000$. The C$\cdots$C bond length used was 1.54 Å and the C–H bond length was 1.08 Å.

III. RESULTS

A. Configurational Interaction

In Table I are given the results for the calculation of the hyperfine coupling based on spin polarization terms alone using the excited configurations χ_2, χ_3. The immediate observation is that the coupling constants do not agree with experiment because they are much too small and take on both negative and positive values, depending on the magnitude of θ (i.e., the conformation). Table II contains the contributions to the hyperfine coupling when all six configurations are included. For in-plane protons, $\theta = \pi/2$, and matrix elements connecting the electron exchange configurations with those describing spin polarization vanish. So the complete CI results already appear in Table I for this angle.

From the results of Tables I and II it is possible to evaluate the constants B_0 and B_2. The value of A_β calculated with $\theta = \pi/2$ is associated with the value of B_0, i.e., $B_0 = 2.64$ G. If Eq. (2) is assumed to provide a satisfactory representation of the hyperfine coupling, the full CI calculation yields

$$\theta = 0; \qquad B_0 + B_2 = 52.85$$

and

$$\theta = \pi/4; \qquad B_0 + (B_2/2) = 27.78.$$

TABLE II. Contributions to the hyperfine coupling constant arising from the inclusion of all configurations in the CI calculation.

θ^a	i	j	Hyperfine factor Ω_{ij}	C_i	C_j	Contribution to hyperfine coupling constant (G)
0	1	1	0.3133×10^{-2}	0.8987	0.8987	1.2830
	1	2	0	0.8987	0.3708	0
	1	3	0.5664	0.8987	0.2835×10^{-1}	7.3187
	1	4	0.7145×10^{-1}	0.8987	-0.2319	-7.5519
	1	5	0.3041×10^{-1}	0.8987	0.1181×10^{-1}	0.1637
	1	6	0	0.8987	0.1198×10^{-1}	0
	2	2	0.3133×10^{-2}	0.3708	0.3708	0.2185
	2	3	0.7704	0.3708	0.2835×10^{-1}	4.1076
	2	4	0.2151×10^{-1}	0.3708	-0.2319	-0.9380
	2	5	-0.5052×10^{-1}	0.3708	0.1181×10^{-1}	-0.1122
	2	6	0.2151×10^{-1}	0.3708	0.1198×10^{-1}	0.0484
	3	3	1.2823	0.2835×10^{-1}	0.2835×10^{-1}	0.5227
	3	4	-0.1242×10^{-1}	0.2835×10^{-1}	-0.2319	0.0414
	3	5	-0.2917×10^{-1}	0.2835×10^{-1}	0.1181×10^{-1}	-0.0050
	3	6	-0.1242×10^{-1}	0.2835×10^{-1}	0.1198×10^{-1}	-0.0021
	4	4	1.6297	-0.2319	-0.2319	44.4505
	4	5	0	-0.2319	0.1181×10^{-1}	0
	4	6	0	-0.2319	0.1198×10^{-1}	0
	5	5	0.2953	0.1181×10^{-1}	0.1181×10^{-1}	0.0209
	5	6	0.6937	0.1181×10^{-1}	0.1198×10^{-1}	0.0497
	6	6	1.6297	0.1198×10^{-1}	0.1198×10^{-1}	0.1185
						Sum = 52.86
45	1	1	0.1546×10^{-2}	0.9108	0.9108	0.6502
	1	2	0	0.9108	0.3792	0
	1	3	0.5664	0.9108	0.1451×10^{-1}	3.7973
	1	4	0.5019×10^{-1}	0.9108	-0.1623	-3.7630
	1	5	-0.2136×10^{-1}	0.9108	0.7597×10^{-2}	-0.0750
	1	6	0	0.9108	0.8530×10^{-2}	0
	2	2	0.1546×10^{-2}	0.3792	0.3792	0.1127
	2	3	0.7704	0.3792	0.1451×10^{-1}	2.1501
	2	4	-0.1511×10^{-1}	0.3792	-0.1623	0.4715
	2	5	-0.3549×10^{-1}	0.3792	0.7597×10^{-2}	-0.0518
	2	6	-0.1511×10^{-1}	0.3792	0.8530×10^{-2}	-0.0248
	3	3	1.2828	0.1451×10^{-1}	0.1451×10^{-1}	0.1370
	3	4	0.8722×10^{-2}	0.1451×10^{-1}	-0.1623	-0.0104
	3	5	-0.2049×10^{-1}	0.1451×10^{-1}	0.7597×10^{-2}	-0.0011
	3	6	0.8722×10^{-2}	0.1451×10^{-1}	0.8530×10^{-2}	0.0005
	4	4	1.6297	-0.1623	-0.1623	21.7774
	4	5	0	-0.1623	0.7597×10^{-2}	0
	4	6	0	-0.1623	0.8530×10^{-2}	0
	5	5	0.2953	0.7597×10^{-2}	0.7597×10^{-2}	0.0086
	5	6	0.6937	0.7597×10^{-2}	0.8530×10^{-2}	0.0228
	6	6	1.6297	0.8530×10^{-2}	0.8530×10^{-2}	0.0601
						Sum = 27.78

a For $\theta = \pi/2$ see Table I.

Solution of these two equations gives $B_0 = 2.71$ G and $B_2 = 50.14$ G. In the full CI calculation, the dominant contribution to the hyperfine coupling for those out-of-plane configurations considered, arises from the "charge transfer" term $\langle \chi_4 \mid H_F \mid \chi_4 \rangle$, with considerably smaller estimates arising from the cross terms $\langle \chi_1 \mid H_F \mid \chi_3 \rangle$ and $\langle \chi_1 \mid H_F \mid \chi_4 \rangle$. These very nearly cancel for the particular basis set used here. While other orthogonalization schemes will alter the relative magnitudes of the cross terms, the facts that emerge are that the charge transfer contribution is the dominant term except at large θ (or $\pi/2$) and the relative contributions of spin polarization, ($\langle \chi_1 \mid H_F \mid \chi_3 \rangle$), and charge transfer to the total hyperfine coupling will remain

roughly the same. Thus valid comparison can still be made to earlier work investigating the mechanisms of hyperfine coupling.

The method we have followed to obtain the results in Table II immediately suggests that a good approximation for B_2 of Eq. (2) may be obtained by considering the electron transfer configuration χ_4 as being the only excited state entering the CI scheme and that it alone gives rise to angular-dependent hyperfine coupling. This is the charge transfer (CT) model, which may hopefully be of practical use to EPR spectroscopists.

B. Charge Transfer Model

If the electron transfer state χ_4 is going to be the sole contributor to the total hyperfine coupling it will be necessary to determine what fraction of the total wavefunction must be attributed to this configuration. That is to say in a function such as

$$\Psi = u_1\chi_1 + u_2\chi_2 \tag{20}$$

it will be necessary to estimate $u_2{}^2$. The total hyperfine coupling is then given in the above approximation by

$$A_\beta = 507.1\Omega_{44} \cos^2\omega/2, \tag{21}$$

where

$$\omega = \text{arccot}\{(W_1 - W_4)/2 \mid W_{14}\mid\}. \tag{22}$$

In Eq. (21), $\cos^2(\omega/2)$ is equivalent to the coefficient $u_2{}^2$, and in Eq. (22) $W_1 = \langle\chi_1\mid H\mid\chi_1\rangle$, $W_4 = \langle\chi_4\mid H\mid\chi_4\rangle$, and $W_{14} = \langle\chi_1\mid H\mid\chi_4\rangle$. It is now possible to express Eq. (21) in terms of the angular variable θ of Eq. (1). The details are outlined in the Appendix. The result is

$$A_\beta = 507.1\Omega_{44}(\lambda_3/\lambda_5)^2 \cos^2\theta, \tag{23}$$

where λ_3 and λ_5 are coefficients which depend on the geometry, expressions for which are also given in the Appendix. Equation (23) represents the first term of a power series in θ while the next few terms are given by

$$A_\beta = 507.1\Omega_{44}(\lambda_3/\lambda_5)^2 \cos^2\theta\{1 - 3(\lambda_3/\lambda_5)^2 \cos^2\theta$$
$$+ 10(\lambda_3/\lambda_5)^4 \cos^4\theta - \cdots\}. \tag{24}$$

Equation (24) may be replaced by the more exact expression, Eq. (21), where

$$\cos^2(\omega/2) = \tfrac{1}{2}\{1 + \text{sgn}F(\theta)[1 + F(\theta)^{-2}]^{-1/2}\} \tag{25}$$

and $F(\theta)$ is a function of the geometry as described in the Appendix.

In the CT model approximation, Eq. (23), the first two terms of Eq. (24), and the more exact (25) are evaluated in Table III for $10°$ intervals between $\theta = 0$ and $\theta = \pi/2$. The values for the λ_i are given in the Appendix. For the particular geometry assumed here, $B_2 = 507.1\Omega_{44}(\lambda_3/\lambda_5)^2 = 67.08$ G. Including the first two terms of Eq. (24) gives

$$A_\beta = B_2 \cos^2\theta + B_4 \cos^4\theta, \tag{26}$$

where B_4 has the value -16.33 G.

IV. DISCUSSION

It is evident from Table II that the dominant mechanistic contribution is charge transfer from the π center to the C–H bond as required for the CT model. Electron transfer to the π center is observed to be fairly minor by comparison. From Table I it may be observed that spin polarization makes only a secondary contribution to the over-all hyperfine coupling. However, the results of the complete CI calculation clearly illustrate that spin polarization is not of secondary importance but a fortuitous cancellation occurs between the cross terms $\langle\chi_1\mid H_F\mid\chi_3\rangle$ and $\langle\chi_1\mid H_F\mid\chi_4\rangle$, which suggests an approximate treatment of the main electron transfer term is appropriate as outlined in the Appendix. The inclusion of the term $\langle\chi_1\mid H_F\mid\chi_4\rangle$ in this simple charge transfer description would be unjustified since the corresponding $\langle\chi_1\mid H_F\mid\chi_3\rangle$ term is also omitted. The expression, Eq. (25), or the approximate form Eqs. (23) and (24) are only really satisfactory for small θ, since $\langle\chi_1\mid H_F\mid\chi_4\rangle \to 0$ as $\theta \to \pi/2$; $\langle\chi_1\mid H_F\mid\chi_3\rangle$ similarly decreases but does not vanish. Hence there would be a finite coupling (i.e., a B_0 term) even when $\langle\chi_1\mid H_F\mid\chi_4\rangle$ and $\langle\chi_4\mid H_F\mid\chi_4\rangle$ vanish. It should also be stressed that these results apply to only the particular orthogonalization scheme followed here as other methods would modify these matrix elements to some extent.

The work reported here supports the general conclusion established by the simple calculations of Colpa and de Boer[6] as opposed to the conclusions reached by Luz.[7] His calculations greatly overestimate the contribution of spin polarization to the hyperfine coupling. Apart from the inherent approximations contained in the formalism employed by Luz and use of estimated integral values, his scheme does not include matrix elements describing polar structures. Since the term Ω_{44} will be large and Ω_{13} small, regardless of the method of orthogonalization, this is a serious deficiency in his calculations. Furthermore as the CI calculations show, some of the terms representing spin polarization and cross terms between the ground configuration and the electron exchange state are of opposite sign and tend to cancel in their contribution to the total coupling. This may be a poor assumption as it is found from the CI calculations that cross terms representing spin polarization and electron exchange with the ground state are equally important, but of opposite sign. For more distant protons along an aliphatic chain, the general approach of Luz should prove to be more satisfactory provided conformational difficulties do not arise as with the long-range coupling observed in numerous systems such as the bicyclic radicals.[8] Exchange polarization for distant protons would be small although possibly still of comparable magnitude to long-range charge transfer.

Stone and Maki[14] have discussed Eq. (2) from the classical and quantum mechanical viewpoint. These authors have proposed that the term B_0 may be attributed to torsional motion of the β protons, and sug-

gest that for a system such as $CH_3-\dot{C}HCOOH$ in irradiated α-alanine at 77°K that the β protons are not rigidly fixed, and the methyl group occupies some of its low torsional energy levels at this temperature. Stone and Maki's proposal that the B_0 term arises from torsional oscillations is not entirely necessary since spin polarization mechanisms can easily lead to hyperfine couplings of the observed magnitude.

Clough, Starr, and McMillan[15] have found that free rotation of the methyl group is still occurring for temperatures as low as 77°K for γ-irradiated single crystals of methylmalonic acid. However, below about 60°K tunneling occurs and only the lowest torsional levels will be involved. For other radicals it has been suggested that rotation of the methyl group is frozen at temperatures around 80°K.[16] To distinguish the importance of these two effects it would be interesting to see temperature-dependent studies in the range 4–77°K performed on the appropriate radicals such as $CH_3-\dot{C}HCOOH$. Below 77°K torsional oscillations should be effectively reduced to a negligible amount; so if hyperfine coupling remains unaltered, B_0 may be assigned to a spin polarization mechanism. It is, however, necessary that any torsional motion cease before the "onset of tunneling" which has been studied recently at 4°K.[15,17,18]

The value of B_2 found for Eq. (23) is somewhat larger than that which is usually found to best fit the experimental results[3] and stems from truncation of the series expansion [Eq. (A18)] at the first term. The inclusion of the second term rectifies this situation so as to agree with experimental results, but the weighting factor of the $\cos^4\theta$ is now much larger than would be expected. This is seen by fitting the CI results for the three orientations to the formula $B_0 + B_2 \cos^2\theta + B_4 \cos^4\theta$, whereby one obtains $B_0 = 2.64$ G, $B_2 = 50.35$ G, and $B_4 = -0.14$ G. Thus the large value of B_2 obtained in the approximate expansion results from the large magnitude of the factor $1/F(\theta)$. The over-all simplicity of the charge transfer model and the fairly good results obtained [cf. Eq. (25) and CI results of Table III] make this a suitable approximation for calculating β-proton hyperfine coupling constants. The fact that Eq. (2) represents a reasonable approximation for computation of the hyperfine coupling can be seen from calculated values of B_0 for the data at $\theta = 0$ and $\pi/4$ compared with the B_0 value at $\theta = \pi/2$ as given at the beginning of the Results section. The very minor disagreement between the different B_0 values supports the idea that Eq. (2) should amount to a fairly good approximation. The calculated values of B_0 and B_2 based on the CI results are reasonably consistent with other values quoted in the literature. For instance in the case of L-alanine, with $\cos\theta = 0.61$, our value of B_0 and B_2 leads to a calculated coupling constant of 21.4 G in fairly close agreement with the experimental value of 18.8 G.[19]

The main factor lacking in the present treatment is the indirect spin polarization mechanism corresponding to consecutive polarization of the C–C σ bond followed by spin decoupling of the C–H σ electrons. Colpa and de Boer have made a crude estimate of this contribution and found it to be approximately one-third the value of the direct contribution, but with the opposite sign. Compared to the contributions from other terms, this amounts to a fairly unimportant correction since as already noted the direct contact contribution is small. The effect of neglecting doubly excited configurations is more difficult to estimate. Considering the very small contributions made by some of the singly excited configurations, it is unlikely that the collective contributions of doubly excited configurations could amount to more than about 0%–10% of the observed hyperfine coupling.

In view of these facts it is felt that this nonempirical calculation which neglects only three-center integrals is at least internally consistent, uses a complete configurational set, and gives quite good results for β-methyl and β-methylene coupling constants. Extended Huckel treatments which neglect spin polarization terms[20] or use symmetry-adapted C–H σ orbitals completely circumvent Eq. (2) and give no insight into the use of this equation as a spectroscopic tool. The over-all simplification which results in Eqs. (21), (23), and (25) can be justified by the results in Table III. They represent practical approximations for use in unusual experimental situations such as where β-methylene protons are displaced from the tetrahedral angle by constraints imposed by the molecular geometry.

TABLE III. Calculated values of the isotropic hyperfine coupling constant for β protons as a function of θ for different levels of approximation.

Angle θ	A_β [Eq. (23)]	A_β [Eq. (24)]	A_β [Eq. (25)]	A_β (CI)
0	67.08	50.75	53.91	52.86
10	65.05	49.69	52.59	
20	59.23	46.50	48.71	
30	50.31	41.12	42.49	
40	39.36	33.74	34.40	
45	33.54	29.46	29.86	27.78
50	27.71	24.93	25.15	
60	16.77	15.75	15.79	
70	7.85	7.62	7.63	
80	2.02	2.01	2.01	
90	0	0	0	2.64

APPENDIX

The following notation for integrals is employed:

$$\langle \phi_a \mid h \mid \phi_b \rangle = \int \phi_a(i) \left[-\tfrac{1}{2}\nabla_i^2 - \sum_\alpha (Z_\alpha/r_{\alpha i}) \right] \phi_b(i) \, d\tau_i \tag{A1}$$

and

$$[\phi_a \phi_b \phi_c \phi_d] = \int \phi_a(i) \phi_b(i) (r_{ij})^{-1} \phi_c(j) \phi_d(j) \, d\tau_i d\tau_j, \tag{A2}$$

where the subscripts denote the centers on which the orbitals are located. The following convenient notation for the atomic orbitals has been employed:

$$\pi=2p_{x2}, \qquad \bar{\pi}=2p_{x3},$$
$$\pi'=2p_{y2}, \qquad k=1s_1,$$
$$\sigma=2p_{z2},$$
$$s=2s_2, \tag{A3}$$

To obtain the result given in Eq. (23) the angular dependence of the factor $\frac{1}{2}(W_1-W_4)/|W_{14}|$ is required. In order to obtain a simple expression for this angular dependence it is necessary to neglect all three-center integrals. In this case $\frac{1}{2}(W_1-W_4)/|W_{14}|$, which is denoted $F(\theta)$, can be written

$$F(\theta)=\frac{1}{2}\{2[\Pi\Pi\sigma_b\sigma_b]+[\sigma_b\sigma_b\sigma_b\sigma_b]-[\Pi\sigma_b\Pi\sigma_b]$$
$$+\langle\Pi|h|\Pi\rangle+2\langle\sigma_b|h|\sigma_b\rangle-\langle\chi_4|H|\chi_4\rangle\}$$
$$\times|\{2[\Pi\sigma_a\sigma_b]-[\Pi\sigma_b\sigma_a]+\langle\Pi|h|\sigma_a\rangle\}|^{-1}. \tag{A4}$$

It is convenient to define the following parameters in terms of atomic orbitals:

$$\alpha_1=\{[1+(a^2/r^2)]^{-1/2}\langle p_z''|k\rangle$$
$$+(3^{1/2}/2)\langle\pi|\bar{\pi}\rangle\}[2(1+S)]^{-1/2},$$
$$\alpha_2=\{[1+(a^2/r^2)]^{-1/2}\langle p_z''|k\rangle$$
$$-(3^{1/2}/2)\langle\pi|\bar{\pi}\rangle\}[2(1-S)]^{-1/2},$$
$$\alpha_3=[1+(a^2/r^2)]^{-1/2}[p_z''kkk],$$
$$\alpha_4=(3^{1/2}/8)\cos\psi\{2[\bar{\pi}s\pi s]+[\bar{\pi}\pi ss]+3[\bar{\pi}\pi\pi'\pi']\}$$
$$+\tfrac{3}{8}\sin2\psi\{[\bar{\pi}s\pi\sigma]+[\bar{\pi}\pi s\sigma]\},$$
$$\alpha_5=(3^{3/2}/8)\cos^2\psi\{[\bar{\pi}\pi\pi\pi]-[\bar{\pi}\pi\pi'\pi']\},$$
$$\alpha_6=[1+(a^2/r^2)]^{-1}[\pi''\pi''kk],$$
$$\alpha_7=[1+(a^2/r^2)]^{-1}\{[p_z''p_z''kk]-[\pi''\pi''kk]\},$$
$$\alpha_8=\tfrac{1}{4}[\bar{\pi}\pi ss]+(3^{1/2}/2)\sin\psi[s\sigma\pi\bar{\pi}]+\tfrac{3}{4}\cos^2\psi[\bar{\pi}\pi\pi'\pi']$$
$$+\tfrac{3}{4}\sin^2\psi[\bar{\pi}\pi\sigma\sigma],$$
$$\alpha_9=\tfrac{3}{4}\cos^2\psi\{[\bar{\pi}\pi\pi\pi]-[\bar{\pi}\pi\pi'\pi']\},$$
$$\alpha_{10}=[1+(a^2/r^2)]^{-1}[\pi''k\pi''k],$$
$$\alpha_{11}=[1+(a^2/r^2)]^{-1}\{[p_z''kp_z''k]-[\pi''k\pi''k]\},$$
$$\alpha_{12}=\tfrac{1}{4}[\bar{\pi}s\bar{\pi}s]+(3^{1/2}/2)\sin\psi[\bar{\pi}s\bar{\pi}\sigma]+\tfrac{3}{4}\cos^2\psi[\bar{\pi}\pi'\bar{\pi}\pi']$$
$$+\tfrac{3}{4}\sin^2\psi[\bar{\pi}\sigma\bar{\pi}\sigma],$$
$$\alpha_{13}=\tfrac{3}{4}\cos^2\psi\{[\bar{\pi}\pi\bar{\pi}\pi]-[\bar{\pi}\pi'\bar{\pi}\pi']\},$$
$$\alpha_{14}=\langle\bar{\pi}|-\nabla^2/2|\bar{\pi}\rangle-\langle\bar{\pi}\bar{\pi}Z_3/r_3\rangle-\langle\bar{\pi}\bar{\pi}Z_2/r_2\rangle$$
$$-\langle\pi''\pi''Z_1/r_1\rangle[1+(a^2/r^2)]^{-1},$$
$$\alpha_{15}=[1+(a^2/r^2)]^{-1}\{\langle\pi''\pi''Z_1/r_1\rangle-\langle p_z''p_z''Z_1/r_1\rangle\},$$
$$\alpha_{16}=[1+(a^2/r^2)]^{-1/2}\{\langle p_z''|-\nabla^2/2|k\rangle$$
$$-\langle p_z''kZ_1/r_1\rangle-\langle p_z''kZ_3/r_3\rangle\},$$
$$\alpha_{17}=(3^{1/2}/2)\cos\psi\{\langle\bar{\pi}|-\nabla^2/2|\pi\rangle$$
$$-\langle\bar{\pi}\pi Z_3/r_3\rangle-\langle\bar{\pi}\pi Z_2/r_2\rangle\}, \tag{A5}$$

where ψ is the angle shown in Fig. 1, $r=1.08\cos\psi$ and $a=1.54+1.08\sin\psi$. The angle ψ has been taken as 19°28' for the present calculations. The double prime which occurs over some of the above atomic orbitals is for the axis system oriented so that the new z axis, z'', is directed along the C_3–H_1 direction.

The desired angular dependence is then obtained in a straightforward manner. Thus

$$[\Pi\Pi\sigma_b\sigma_b]=\tau_9+\tau_{10}\cos^2\theta+\tau_8\cos^4\theta, \tag{A6}$$
$$[\Pi\sigma_b\Pi\sigma_b]=\tau_6+\tau_7\cos^2\theta+\tau_8\cos^4\theta, \tag{A7}$$
$$[\Pi\sigma_a\sigma_b]=\tau_1\cos\theta+\tau_2\cos^3\theta, \tag{A8}$$
$$[\Pi\sigma_b\sigma_a]=\tau_3\cos\theta+\tau_2\cos^3\theta, \tag{A9}$$
$$\langle\Pi|h|\Pi\rangle=\tau_5\cos^2\theta+\alpha_{14}, \tag{A10}$$
$$\langle\Pi|h|\sigma_a\rangle=\tau_4\cos\theta, \tag{A11}$$

wherein

$$\tau_1=\{\alpha_3-\alpha_4\}\{2(1+S)[2(1-S]^{1/2}\}^{-1}-\alpha_1[\sigma_b\sigma_b\sigma_a]$$
$$-\alpha_2[\sigma_a\sigma_a\sigma_b\sigma_b],$$
$$\tau_2=-\alpha_5\{2(1+S)[2(1-S)]^{1/2}\}^{-1}=\lambda_4, \tag{A12}$$
$$\tau_3=\{\alpha_3-\alpha_4\}\{2(1+S)[2(1-S)]^{1/2}\}^{-1}$$
$$-\alpha_1[\sigma_b\sigma_b\sigma_b\sigma_a]-\alpha_2[\sigma_a\sigma_b\sigma_a\sigma_b],$$
$$\tau_4=\{\alpha_{16}-\alpha_{17}\}\{2(1-S)\}^{-1/2}-\alpha_1\langle\sigma_b|h|\sigma_a\rangle$$
$$-\alpha_2\langle\sigma_a|h|\sigma_a\rangle,$$
$$\tau_5=\alpha_{15}+\alpha_1^2\langle\sigma_b|h|\sigma_b\rangle+\alpha_2^2\langle\sigma_a|h|\sigma_a\rangle$$
$$+2\alpha_1\alpha_2\langle\sigma_b|h|\sigma_a\rangle-2\alpha_1\{\alpha_{16}+\alpha_{17}\}\{2(1+S)\}^{-1/2}$$
$$-2\alpha_2\{\alpha_{16}-\alpha_{17}\}\{2(1-S)\}^{-1/2},$$
$$\tau_6=\{\alpha_{10}+\alpha_{12}\}\{2(1+S)\}^{-1},$$
$$\tau_7=\{\alpha_{11}+\alpha_{13}\}\{2(1+S)\}^{-1}+\alpha_1^2[\sigma_b\sigma_b\sigma_b\sigma_b]$$
$$+\alpha_2^2[\sigma_b\sigma_a\sigma_b\sigma_a]+2\alpha_1\alpha_2[\sigma_b\sigma_b\sigma_b\sigma_a]$$
$$-2\alpha_1\{\alpha_3+\alpha_4\}\{2(1+S)\}^{-3/2}$$
$$-2\alpha_2\{\alpha_3-\alpha_4\}\{2(1+S)[2(1-S)]^{1/2}\}^{-1},$$
$$\tau_8=\lambda_2=2\alpha_2\alpha_5\{2(1+S)[2(1-S)]^{1/2}\}^{-1}$$
$$-2\alpha_1\alpha_5\{2(1+S)\}^{-3/2}, \tag{A13}$$
$$\tau_9=\{\alpha_8+\alpha_6\}\{2(1+S)\}^{-1},$$
$$\tau_{10}=\{\alpha_7+\alpha_9\}\{2(1+S)\}^{-1}+\alpha_2^2[\sigma_b\sigma_b\sigma_a\sigma_a]$$
$$+2\alpha_1\alpha_2[\sigma_b\sigma_b\sigma_b\sigma_a]+\alpha_1^2[\sigma_b\sigma_b\sigma_b\sigma_b]$$
$$-2\alpha_1\{\alpha_3+\alpha_4\}\{2(1+S)\}^{-3/2}$$
$$-2\alpha_2\{\alpha_3-\alpha_4\}\{2(1+S)[2(1-S)]^{1/2}\}^{-1}.$$

Here the α_i are defined by Eq. (A5). If the following

factors are used:

$$\lambda_1 = 2\tau_{10} - \tau_7 + \tau_5, \tag{A14}$$

$$\lambda_3 = 2\tau_1 + \tau_4 - \tau_3, \tag{A15}$$

$$\lambda_5 = 2\tau_9 + \alpha_{14} - \tau_6 + [\sigma_b\sigma_b\sigma_b\sigma_b]$$
$$+ 2\langle\sigma_b \mid h \mid \sigma_b\rangle - \langle\chi_4 \mid H \mid \chi_4\rangle, \tag{A16}$$

Eq. (4) then becomes

$$F(\theta) = \tfrac{1}{2}(\lambda_5 + \lambda_1\cos^2\theta + \lambda_2\cos^4\theta) \mid \lambda_3\cos\theta + \lambda_4\cos^3\theta \mid^{-1}. \tag{A17}$$

These coefficients have the following numerical values:

$$\lambda_1 = 0.318625\times10^{-2}, \qquad \lambda_2 = -0.413264\times10^{-3},$$

$$\lambda_3 = 0.176489, \qquad \lambda_4 = -0.135273\times10^{-2},$$

and

$$\lambda_5 = -0.619515$$

for the values of ψ and bond lengths cited.

Now the coefficient u_2^2 of Eq. (20) is given by

$$\cos^2(\omega/2) = \tfrac{1}{2}\{1 + \mathrm{sgn}F(\theta)[1 + F(\theta)^{-2}]^{-1/2}\}. \tag{A18}$$

Since λ_1, λ_2, and λ_4 are small $F(\theta)$ may be approximated to

$$F(\theta) = \lambda_5/2 \mid \lambda_3\cos\theta \mid \tag{A19}$$

and hence

$$\cos^2(\omega/2) \approx (\lambda_3^2/\lambda_5^2)\cos^2\theta. \tag{A20}$$

In order to establish values of B_2 for different geometries (e.g., different hybridization or different bond lengths) it is simply necessary to calculate the α_i and τ_i coefficients (the $3^{1/2}$ factor in the expressions for α_i will be changed for different hydridizations), obtain new values of λ_i according to Eqs. (A12)–(A16), and determine a new value of $F(\theta)$ for use in Eq. (A18). If only small changes are necessary then the approximate expression for $F(\theta)$, [Eq. (A19)], is satisfactory and this reduces the required number of α_i and τ_i coefficients by approximately half.

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