

# VECTOR MODEL FOR INDIRECT PROTON HYPERFINE INTERACTIONS IN $\pi$ -ELECTRON RADICALS\*

BY HARDEN M. MCCONNELL

GATES AND CRELLIN LABORATORIES OF CHEMISTRY,†  
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA 4, CALIFORNIA

*Communicated by Richard M. Badger, June 24, 1957*

Significant information on unpaired electron distributions in molecules, liquids, and solids can sometimes be obtained from magnetic resonance studies of electron-nucleus hyperfine interactions. A particularly important problem in this field involves the proton hyperfine interactions that have been observed in the electron magnetic resonance spectra of a large number of aromatic radicals in solution.<sup>1-3</sup> The problem concerns the theoretical basis for a proposal that the observed hyperfine splitting  $a_N$  due to aromatic proton  $N$  in an aromatic radical can be used to estimate the unpaired spin density  $\rho_N$  at carbon atom  $N$  to which proton  $N$  is attached, according to the equation<sup>2, 4-6</sup>

$$a_N = Q \rho_N. \quad (1)$$

A semiempirical value of  $Q$  derived from observed splittings  $a_N$  and theoretically calculated spin densities  $\rho_N$  is  $-30 \pm 5$  gauss, or  $-85 \pm 15$  Mc.<sup>2</sup> Equation (1) has been derived recently using molecular orbital theory with arbitrary  $\pi$ - $\pi$  configuration interaction.<sup>6</sup> We show here how the simple proportionality in equation (1) may be derived using the Dirac vector model.

Let  $\mathbf{S}_h$ ,  $\mathbf{S}_\sigma$ ,  $\mathbf{S}_\pi$  be the spin vector operators for electrons  $h$ ,  $\sigma$ ,  $\pi$ . Electron  $h$  is a  $1s$  hydrogen atomic orbital centered on aromatic proton  $N$ . Electron  $\sigma$  is in the  $sp^2$  hybrid orbital centered on carbon atom  $N$  and directed toward aromatic proton  $N$ . Electron  $\pi$  is in a  $2p_z\pi$  orbital centered on carbon atom  $N$ . The nodal plane of the  $2p_z\pi$  orbital passes through proton  $N$ . Let  $|n^\circ\rangle$  be a basic set of spin eigenfunctions including both  $\sigma$  and  $\pi$  electrons. Assume the Hamiltonian matrix  $H_{mn}^\circ$  to be diagonal with respect to the set  $|n^\circ\rangle$  except for nondiagonal terms due to  $\sigma$ - $\pi$  exchange coupling. Treat this  $\sigma$ - $\pi$  interaction as a first-order perturbation on the ground-state spin function,  $|0^\circ\rangle$ :

$$\mathfrak{H}^{(1)} = \text{const.} - \frac{1}{2}(1 + 4\mathbf{S}_\sigma \cdot \mathbf{S}_\pi)J_{\sigma\pi}. \quad (2)$$

In equation (2)  $J_{\sigma\pi}$  is the exchange integral between electrons  $\sigma$  and  $\pi$ . To first order, the exact ground-state spin function  $|0\rangle$  is

$$|0\rangle = |0^\circ\rangle + 2J_{\sigma\pi} \sum_n \frac{\langle n^\circ | \mathbf{S}_\sigma \cdot \mathbf{S}_\pi | 0^\circ \rangle}{\Delta E_n^\circ} |n^\circ\rangle, \quad (3)$$

where  $\Delta E_n^\circ = E_n^\circ - E_0^\circ$ . We use  $|0\rangle$  in equation (3) to calculate the hyperfine splitting due to proton  $N$ , which is

$$a_N = a_H^\circ \frac{\langle 0 | S_{hz} | 0 \rangle}{S_z}. \quad (4)$$

Here, in standard notation,<sup>5, 6</sup>

$$a_H^\circ = \frac{8\pi g |\beta| \mu_H}{3h I_H} \quad (5)$$

$$= 1,420 \text{ Mc}$$

and

$$S_z = \langle 0 | \sum_k S_{kz} | 0 \rangle. \quad (6)$$

The sum in equation (6) is over all spins in the molecule. From equations (3) and (4) we obtain, to first order,

$$a_N = \frac{4J_{\sigma\pi} a_H^\circ}{S_z} \sum_n \frac{\langle 0^\circ | \mathbf{S}_\sigma \cdot \mathbf{S}_\pi | n^\circ \rangle \langle n^\circ | S_{hz} | 0^\circ \rangle}{\Delta E_n^\circ}. \quad (7)$$

Explicit calculations show that only a very limited number of  $\sigma$ - $\pi$  excited spin states can contribute to the summation in equation (7), and if we assume that all of these  $\sigma$ - $\pi$  excited states have roughly the same excitation energy,  $\Delta E$ , then equation (7) can be simplified to give

$$a_N = \frac{4J_{\sigma\pi} a_H^\circ}{\Delta E S_z} \langle 0^\circ | \mathbf{S}_\sigma \cdot \mathbf{S}_\pi S_{hz} | 0^\circ \rangle. \quad (8)$$

To evaluate the above diagonal matrix element, we note that if  $|\Pi^\circ\rangle$  is the normalized pure  $\pi$ -electron spin component of  $|0^\circ\rangle$ , then the  $\sigma$  component contains the factor  $(\alpha(\mathfrak{h}) \beta(\mathfrak{h}) - \beta(\mathfrak{h}) \alpha(\mathfrak{h}))/\sqrt{2}$ , and when the integrations over the spin variables of  $\mathfrak{h}$  and  $\sigma$  (and the other  $\sigma$  electrons) are carried out, we obtain

$$a_N = - \left( \frac{J_{\sigma\pi}}{\Delta E} \right) a_H^\circ \frac{\langle \Pi^\circ | S_{\pi z} | \Pi^\circ \rangle}{S_z}. \quad (9)$$

Since  $\rho_N = \langle \Pi^\circ | S_{\pi z} | \Pi^\circ \rangle / S_z$ ,<sup>6</sup> we obtain equation (1) from equation (9) when  $Q = -J_{\sigma\pi} a_H^\circ / \Delta E$ . Previous calculations indicate  $J_{\sigma\pi} / \Delta E$  to be of the order of magnitude of 0.1, so that this theoretical value of  $Q$  is in order-of-magnitude agreement with the semiempirical value.<sup>5</sup>

The critical step in the present derivation of equation (1) is the assumption of an approximately constant  $\Delta E \approx \Delta E_n^\circ$  for all the interacting states  $|n^\circ\rangle$  in equation (7). A sufficient condition for the validity of this assumption is that all  $\pi$ - $\pi$  electron exchange integrals with magnitude  $|J_{\pi\pi}|$  are very small compared with the CH bond integral  $|J_{\sigma h}|$ . In this case  $\Delta E_n^\circ$  is determined by  $J_{\sigma\pi}$  alone. It is significant that the conditions we find here for the validity of equation (1) using the vector model are compatible with the molecular orbital derivation of equation (1), with arbitrary  $\pi$ - $\pi$  configuration interaction.<sup>6</sup> In both cases the single proportionality between spin density and proton hyperfine splitting in equation (1) becomes exact as  $|J_{\sigma\pi}| / |J_{\pi\pi}| \rightarrow 0$  and  $|J_{\pi\pi}| / |J_{\sigma h}| \rightarrow 0$ . Detailed calculations, including nonorthogonality effects, are of course required to test the adequacy of these limiting approximations.

\* Supported in part by the Office of Ordnance Research, U.S. Army.

† Contribution No. 2214.

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<sup>5</sup> H. M. McConnell, *J. Chem. Phys.*, **24**, 764, 1956.  
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## CRITIQUE OF THE THEORY OF OPTICAL ACTIVITY OF HELICAL POLYMERS

BY WILLIAM MOFFITT

DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY

AND

DONALD D. FITTS\* AND JOHN G. KIRKWOOD

STERLING CHEMISTRY LABORATORY,† YALE UNIVERSITY

Communicated June 10, 1957

1. *Introduction.*—In a series of recent articles,<sup>1-4</sup> we have severally attempted to use coupled-oscillator theory in order to understand the optical activity of polypeptides. This approach, the development of which stems from Born<sup>5</sup> and Kuhn,<sup>6</sup> was first used in quantum mechanics by Kirkwood<sup>7</sup> as the basis for his polarizability theory of rotatory power. In recent months we have been clarifying the relationship between our respective treatments, leaving out of account differences which stem from the specific means by which we have attained tractability. As a result, we have been able to show that a general formula, derived by Kirkwood<sup>7</sup> under special (nondegenerate) conditions which do not apply to polymers, has a wider range of validity and may also be used in the present context. But, paradoxically enough, we have thereby found an error in Moffitt's work,<sup>3</sup> one of the purposes of which was to acknowledge explicitly the degenerate nature of this problem.

In the following section, Kirkwood's formula is rederived under conditions appertaining to a sequence of identical residues. And in a final section this prescription is more specifically applied to helices. Some discussion is given of the way in which the result may be used. It appears that a particularly important factor ( $A_{\sigma\sigma}$ ) is composed of two terms, one of which ( $A_{\sigma\sigma}^{(1)}$ ) was correctly assessed by Moffitt, whereas the other ( $A_{\sigma\sigma}^{(2)}$ ) was absent from his earlier derivation. The reason for this omission is analyzed and shown to originate, somewhat unexpectedly, in the failure of the Born-von Kármán boundary conditions which he had used in the course of his exciton treatment.

We are forced to conclude that the close agreement between the data presented by Moffitt and Yang,<sup>3</sup> and Moffitt's calculations for the  $\alpha$ -helix,<sup>4</sup> is illusory and does not enable a definite screw sense to be assigned to these polypeptides. Moffitt's calculations were based on certain  $A_{\sigma\sigma}^{(1)}$  terms alone, and our estimates indicate that the corresponding  $A_{\sigma\sigma}^{(2)}$  contributions are of the same order but of opposite sign. However, since the qualitative form of the dispersion shown by the various partial rotations was correctly described in his work, this quantitative failure in no way vitiates the empirical correlations put forward by Moffitt and Yang; any