

McConnell H M & Strathdee J. Theory of anisotropic hyperfine interactions in  $\pi$ -electron radicals. *Mol. Phys.* 2:129-38, 1959.

[Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, and Shell Development Co., Emeryville, CA]

Paramagnetic resonance spectroscopy can be used to obtain remarkably detailed information on the electronic structures of free radicals, organic molecules in triplet states, and certain organic polymers. Experimental values of electron spin distributions on carbon atoms can be used to test theories of molecular electronic structure, such as those involving valence bonds, molecular orbitals, or solitons. The electron spin distributions on carbon atoms can be deduced from experimentally observed (electron-spin)-(proton-spin) hyperfine splittings, together with a theoretical analysis of the relation between proton hyperfine interactions and spin densities on carbon atoms. [The *SCI*® indicates that this paper has been cited in over 420 publications.]

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This paper is essentially a companion to that published with graduate student Don Chesnut at Caltech that developed the theory for isotropic proton hyperfine interactions in paramagnetic organic molecules.<sup>1</sup> The present paper concerns the theory of the anisotropic component of the nuclear hyperfine interaction that is often necessary to interpret the spectra of paramagnetic organic molecules in solids. John Strathdee was a summer employee at Shell Development Company in 1957 and went on to study theoretical physics in Cambridge, England.

I had two motivations for making these theoretical calculations of (electron-spin)-(proton-spin) dipole interactions in organic free radicals (the anisotropic hyperfine interaction). First, it was clear that one needed a quantitative theory of these hyperfine splittings to interpret virtually any paramagnetic resonance spectrum in a condensed system where the

motion of the organic molecule is restricted. Thus, the interpretation of hyperfine splittings from paramagnetic molecules produced by radiation damage in solids, or trapped in rigid glasses, especially when oriented in single crystals, all require a quantitative theory of the relation of anisotropic hyperfine interaction and molecular structure.

The second motivation for working out a quantitative theory for anisotropic proton hyperfine interactions stemmed from the realization that this could provide a critical test of the theory of the isotropic proton hyperfine splitting in  $\pi$ -electron radicals. The theory, developed in some detail with Chesnut, predicted an anomalous (negative) sign for the isotropic coupling constant.<sup>1</sup> Since the *sign* of the (electron-spin)-(proton-spin) dipolar contribution to the total hyperfine interaction can be stated without ambiguity, observed anisotropic hyperfine interactions (dipolar plus isotropic) can be used to determine the sign of the isotropic hyperfine interaction, provided that a reliable theory of the dipolar contribution to the anisotropic interaction is available. The *Classic* paper provided this theory, and subsequent experimental studies of anisotropic hyperfine interactions in the malonic acid radical (COOH)<sub>2</sub> established the validity of the predicted anomalous sign.<sup>2</sup> (Three of the integrals in the *Classic* paper require correction due to a divergence [see R.M. Pitzer *et al.*].<sup>3</sup>) These three integrals are not involved in any of the present discussion.)

My theoretical and experimental studies of nuclear hyperfine interactions in paramagnetic molecular systems were strongly influenced by the elegant early experiments of C. Hutchison, Jr., S.I. Weissman, and G.K. Fraenkel and by later experiments of Chesnut and W.P. Phillips. A recent paper by White *et al.* provides a starting point for some of the most recent literature.<sup>4</sup>

[Professor McConnell will be presented the NAS award in chemical sciences on April 25th.]

- McConnell H M & Chesnut D B. Theory of isotropic hyperfine interactions in  $\pi$ -electron radicals. *J. Chem. Phys.* 28:107-17, 1958. (Cited 790 times.) [See also: McConnell H M. Citation Classic. (Thackray A. comp.) *Contemporary classics in physical, chemical, and earth sciences*. Philadelphia: ISI Press, 1986. p. 238.]
- McConnell H M, Heller C, Cole T & Fessenden R W. Radiation damage in organic crystals. *J. Amer. Chem. Soc.* 82:766-75, 1960. (Cited 315 times.)
- Pitzer R M, Kern C W & Lipscomb W N. Evaluation of molecular integrals by solid spherical harmonic expansions. *J. Chem. Phys.* 37:267-74, 1962. (Cited 130 times.)
- White C T, Kutzler F W & Cook M. Proton Fermi-contact coupling constants from local-density-functional theory: application to the soliton in polyacetylene. *Phys. Rev. Lett.* 56:252-5, 1986.