This Week's Citation Classic

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McLachlan A D. Self-consistent field theory of the electron spin distribution in pi-electron radicals. *Molec. Phys.* **3**:233-52, 1960. [Dept. Theoretical Chemistry, University Chemical Lab., Cambridge, England]

The paper showed how to calculate the electron spin density on the rings of aromatic radicals like the naphthalene negative ion from a simple molecular wave function, using a perturbation formula which allows for negative spin densities. [The ***SCI***® indicates that this paper has been cited over 700 times since 1961.]

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"Electron spin resonance first began to make an impact on organic chemistry in 1956, when Weissman and De Boer[1] published the beautiful hyperfine structure patterns of aromatic hydrocarbon negative ions (benzene, naphthalene, and others) while McConnell[2] laid the foundation of their interpretation, with $a = Qp$. One surprising outcome, which McConnell explained very elegantly with Pauling's valence-bond theory, was that the signs of spin densities could be negative, showing that the local unbalanced spin of the electrons on one atom could be antiparallel to the net spin of the whole radical.

"As a young research student in Cambridge in 1956, I was lucky to be working under H.C. Longuet-Higgins, whose theoretical chemistry group was then one of the great centres of molecular orbital theory, following the tradition of Coulson and Lennard-Jones. There Orgel and Griffith were laying the foundations of transition metal ion theory, while Pople was developing the interpretation of NMR spectra.

"One day, Pople and Longuet-Higgins came in and began talking about spin coupling constants. Suddenly they suggested that I should look into negative spin densities and the hyperfine structure of aromatic methyl groups. This was an exciting challenge, as I knew little about electron spin, and nothing at all about magnetic resonance. After a few weeks immersed in Fermi's paper on contact hyperfine coupling the problem became clearer, and a theory of spin coupling in the methyl group emerged.

"What next? I felt sure that a molecular orbital explanation of negative spin densities was possible. Intuitively it seemed clear that the exchange part of the Hartree-Fock field would affect electrons of alpha and beta spin differently, so that there should be different orbitals for different spins. Luckily Pople, with Nesbet and Brickstock,[3] had just completed the development of the Huckel molecular orbital theory into a self-consistent field method. Their papers suggested how to include exchange effects and obtain negative spin densities. I then realised that the mathematics needed to deal with weak exchange effects had already been developed —Coulson and Longuet-Higgins's mutual pi-electron polarisability. The method was completed and it was exciting to find that the results fitted the hyperfine spectra very nicely, often better than valence-bond theory.

"Why so often cited? I suspect two reasons: one, the need, with an enormous number of pi-electron radicals which give good ESR spectra, numbering many hundreds; the other, it is an easy method usable by even a fairly unsophisticated chemist. A classic? The description is quite harmlessly flattering as long as one takes frequent citation no more seriously than a prize in a beauty contest."

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1. **De Boer E & Weinman S I.** Electron spin resonance spectra of aromatic mononegative and monopositive ions. *J. Amer. Chem. Soc.* **80**:4549-55, 1958.
2. **McConnell H M.** Indirect hyperfine interactions in the paramagnetic resonance spectra of aromatic free radicals. *J. Chem. Phys* **24**:764-6, 1956.
3. **Brickstock A & Pople J A.** Resonance energies and charge distributions of unsaturated hydrocarbon radicals and ions. *Trans. Faraday Soc.* **50**:901-11, 1954.