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Isotropic Hyperfine Interactions in Aromatic Free Radicals*

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It is shown, by a procedure similar to one used by Abragam, Horowitz, and Pryce in their studies of hyperfine structure in paramagnetic ions and atoms, that configurational interaction may contribute to the isotropic hyperfine interaction in free radicals. For a configurational admixture of the type $(\sigma_B)^2(\pi) + \lambda(\sigma_B)(\sigma_A)(\pi)$, the hyperfine interaction is $32\pi/3\sqrt{6}\mu_\eta\mu_e\lambda\sigma_B(\mathbf{r}_\eta)\sigma_A(\mathbf{r}_\eta)$ where μ_e and μ_η are magnetic moments of the electron and the nucleus η , and $\sigma(\mathbf{r}_\eta)$ is the magnitude of the orbital σ at the position of the nucleus. Since the hyperfine coupling is linear in λ , only small admixtures of excited configurations are required to account for the proton hyperfine splittings observed in aromatic free radicals.

THE isotropic hyperfine structure of free radicals is related to the density of unpaired electrons at the positions of the magnetic nuclei in the molecule. For one electron systems, or systems which may be treated as one electron system, this density is given by the square of the electron wave function at the nucleus in question. For many electron atoms or ions it has been recently shown by Abragam, Horowitz, and Pryce¹ that the density may contain products of different one-electron functions, and that these terms may be the predominant ones in producing the hyperfine interaction. These terms arise in connection with admixture of excited configurations and are *linear* in the amplitude of the admixture. Analysis of the behavior of free radicals indicates that certain of the hyperfine structures which have thus far been observed may be accounted for by configurational interaction. This development is in some respects similar to those given by McConnell and Bersohn.²

The experimental results which have given rise to this work consist principally of the observation of a number of instances of hyperfine splitting with protons in aromatic free radicals.³⁻⁹

The unpaired electron in these compounds is assigned to a π orbital which has a node in the plane of the rings. In each instance, however, the protons in the rings contribute to the hyperfine structure. As an example we may cite the naphthalene negative ion. Although the only magnetic nuclei in this free radical are the protons in the plane of the ring, there is a rich hyperfine structure of seventeen lines covering about 30 oersteds.

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¹ Abragam, Horowitz, and Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

² H. McConnell, J. Chem. Phys. **24**, 764 (1956); R. Bersohn, *ibid.* **24**, 1066 (1956).

³ Lipkin, Paul, Townsend, and Weissman, Science **117**, 534 (1953).

⁴ Weissman, Townsend, Paul, and Pake, J. Chem. Phys. **21**, 2227 (1953).

⁵ S. I. Weissman, J. Chem. Phys. **22**, 1135 (1954).

⁶ H. S. Jarrett and G. J. Sloan, J. Chem. Phys. **22**, 1783 (1954).

⁷ B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc. **77**, 2707 (1955).

⁸ R. Hoskins, J. Chem. Phys. **23**, 1975 (1955).

⁹ J. E. Wertz and J. L. Vivo, J. Chem. Phys. **23**, 2193 (1955).

An earlier suggestion⁴ that the splitting in this case might arise from the zero point vibrations of the proton is incorrect. Observations by Fraenkel and Venkataraman¹⁰ of the effect of deuterium substitutions have demonstrated that the splittings are dependent on the magnetic moment of the nucleus but not on its mass.

We now turn to a treatment of the connection between configurational mixing and isotropic hyperfine interaction. The portion of the Hamiltonian operator, H_η , which represents the isotropic hyperfine interaction between nucleus and the electron spin magnetic moments is¹¹

$$H_\eta = \frac{8\pi}{3} \mathbf{u}_\eta \cdot \sum_k \mathbf{u}_k \delta(\mathbf{r}_k - \mathbf{r}_\eta) \quad (1)$$

where \mathbf{u}_η and \mathbf{u}_k are the spin magnetic moment operators for the nucleus and the k th electron. The summation is carried out over all electrons. In a strong magnetic field in the z direction, the important part of the operator becomes

$$\frac{8\pi}{3} \mu_{\eta z} \sum_k \mu_{kz} \delta(\mathbf{r}_k - \mathbf{r}_\eta). \quad (2)$$

The expectation value $\sum_k \mu_{kz} \delta(\mathbf{r}_k - \mathbf{r}_\eta)$ may be called the density of electronic magnetic moment at the position of η . It is this expectation value which is important in the hyperfine interaction. For a configuration $(a_1)^2 \cdots (a_{(n-1)/2})^2 a_{(n+1)/2}$ of n electrons, calculation of the expectation value of (2) shows that the hyperfine interaction depends only on $|a_{(n+1)/2}(\mathbf{r}_\eta)|^2$, the density of the singly occupied orbital at η . The contribution of the filled orbitals vanishes because of the pairing of their spins. As has been mentioned previously, for an aromatic free radical the singly occupied orbital vanishes at the positions of the ring protons.

We now seek a configuration whose admixture will lead to a nonvanishing magnetic moment density at η . Excitation from one of the filled π orbitals to another π orbital will not help, since the magnetic moment density

¹⁰ G. K. Fraenkel and B. Venkataraman, J. Chem. Phys. **24**, 737 (1956).

¹¹ E. Fermi, Z. Physik **60**, 320 (1930).

vanishes for such a configuration as well as for the original one. A configuration in which an occupant of a σ orbital is excited to a π orbital or vice versa is not acceptable, since such a configuration cannot mix with the original configuration because its symmetry with respect to reflection in the aromatic ring is different from that of the original configuration. A configuration in which one occupant of a σ orbital is excited to a second σ orbital yields the desired result. Let us picture the σ orbital from which the excitation takes place as a bonding orbital, σ_B . Let the excitation take place to an antibonding orbital σ_A . (These orbitals need not be specified so explicitly but this designation may correspond fairly well to the situation in aromatic free radicals.) The principal configuration may be designated: (filled orbitals) $(\sigma_B)^2(\pi)$; the excited configuration: (filled orbitals) $(\sigma_B)(\pi)(\sigma_A)$. Since the "filled" orbitals do not contribute in the admixture here described, we need consider only the behavior of the two three-electron configurations $(\sigma_B)^2(\pi)$ and $(\sigma_B)(\pi)(\sigma_A)$.

Corresponding to the state of eigenvalue of $Sz = \frac{1}{2}$, the configuration $(\sigma_B)^2(\pi)$ has the wave function

$$\Phi = \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha\sigma_B(1) & \alpha\sigma_B(2) & \alpha\sigma_B(3) \\ \beta\sigma_B(1) & \beta\sigma_B(2) & \beta\sigma_B(3) \\ \alpha\pi(1) & \alpha\pi(2) & \alpha\pi(3) \end{vmatrix}.$$

Corresponding to $(\sigma_B)(\pi)(\sigma_A)$ there are three functions with eigenvalue of $Sz = \frac{1}{2}$. These are:

$$D_I = \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha\sigma_B(1) & \alpha\sigma_B(2) & \alpha\sigma_B(3) \\ \alpha\sigma_A(1) & \alpha\sigma_A(2) & \alpha\sigma_A(3) \\ \beta\pi(1) & \beta\pi(2) & \beta\pi(3) \end{vmatrix}$$

$$D_{II} = \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha\sigma_B(1) & \alpha\sigma_B(2) & \sigma_B(3) \\ \beta\sigma_A(1) & \beta\sigma_A(2) & \beta\sigma_A(3) \\ \alpha\pi(1) & \alpha\pi(2) & \alpha\pi(3) \end{vmatrix}$$

$$D_{III} = \frac{1}{\sqrt{6}} \begin{vmatrix} \beta\sigma_B(1) & \beta\sigma_B(2) & \beta\sigma_B(3) \\ \alpha\sigma_A(1) & \alpha\sigma_A(2) & \alpha\sigma_A(3) \\ \alpha\pi(1) & \alpha\pi(2) & \alpha\pi(3) \end{vmatrix}.$$

One linear combination of D_I , D_{II} , D_{III} belongs to a quartet state and two to doublet states. One of the doublet states, which can be thought of as arising from a combination of the singlet $(\sigma_B)(\sigma_A)$ state with π leads to no hyperfine interaction. The other, corresponding to combination of the triplet $(\sigma_B)(\sigma_A)$ state with π , is the one we seek. This combination is

$$\Psi = (1/\sqrt{6})[2D_I - (D_{II} + D_{III})].$$

It may be verified by direct calculation that Ψ is an eigenfunction of S^2 with eigenvalue $3/4$.

If we now take as the configurational mixture describing the state of our system

$$\chi = \Phi + \lambda\Psi, \quad \lambda^2 \ll 1$$

we find that the expectation value of H_η

$$\langle \chi | H_\eta | \chi \rangle = \frac{32\pi}{3\sqrt{6}} \lambda \mu_\eta \mu_{\sigma_B}(\mathbf{r}_\eta) \sigma_A(\mathbf{r}_\eta).^\dagger$$

Unusual features of the result are the linear dependence on λ and the fact that the magnetic moment density depends on the product of the probability amplitude at the nucleus of the state from which the electron is excited and the probability amplitude of the state into which it is excited. The result suggests that a "magnetic moment density matrix" may be a useful idea.

In a case of interest to us here, such as naphthalene negative ion, we may consider σ_B and σ_A to be the bonding and antibonding orbitals associated with the CH bonds. Each contains hydrogen 1s components, the antibonding function probably having the greater amplitude of hydrogen 1s component. To account for the hyperfine splitting in naphthalene negative ion a value of λ of the order of 0.1 is required. This does not seem an unreasonably large value. The determination of λ by direct perturbation calculations has not been carried out.

Since σ_B and σ_A are nonvanishing at the positions of the carbon nuclei as well as the hydrogen nuclei, we anticipate an isotropic hyperfine splitting from aromatic free radicals containing C^{13} in the rings. Taking into account the nuclear moment of C^{13} , the probable admixtures of carbon 2s function in σ_B and σ_A , and the value of carbon 2s function at the nucleus, we anticipate that the C^{13} splitting associated with a particular bond should be of the same order that somewhat smaller than the proton splitting. Experiments are under way in this laboratory to test this point.

In connection with this latter point, one may discuss the origin of the splitting observed in triphenylmethyl with C^{13} in the methyl position. The splitting is 26 oersteds.¹² Since the splitting produced by individual protons in triphenylmethyl is at most 3 or 4 oersteds, it is unlikely that the C^{13} splitting arises from admixture of excited configurations. It seems probable that the three central bonds in triphenylmethyl are not coplanar, and that the singly occupied orbital contains sufficient carbon 2s contribution to account for most of the splitting.

[†] It has been assumed that σ_B and σ_A are chosen to be real. If they are complex $\sigma_B\sigma_A$ is replaced by $\frac{1}{2}(\sigma_B^*\sigma_A + \sigma_B\sigma_A^*)$.

¹² S. Weissman and J. Sowden, J. Am. Chem. Soc. **75**, 503 (1953); Weissman, Tuttle, and de Boer, J. Phys. Chem. (to be published).