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# THE METHOD OF MOLECULAR ORBITALS AND SPIN DENSITY IN PARAMAGNETIC RESONANCE

I.D. Morozova

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## INTRODUCTION

The development of the technique of electron paramagnetic resonance and of nuclear magnetic resonance has made it possible to investigate the behaviour of a large number of molecules and free radicals in a magnetic field. Quantum chemistry and one of its techniques, the molecular orbital method, play an important part in the theoretical interpretation of paramagnetic resonance spectra. Application of this method to the study of organic free radicals, molecules in which an unpaired electron is linked with the whole system, *i.e.* is regarded as located in a molecular and not an atomic orbital, can give valuable information about the structure of these compounds.

A large number of free radicals have been studied by the electron paramagnetic resonance method[1-3], and it is of interest to give a theoretical explanation based on the molecular orbital method of new characteristics such as spin density, the magnitude of which can be judged from the hyperfine structure of the electron paramagnetic resonance spectra.

Let us examine briefly the origin of hyperfine structure in the spectra of paramagnetic substances. In an external magnetic field the spin of an unpaired electron is known to acquire two orientations, either in the same or in the opposite direction to the field, corresponding to two energy states, $-\frac{1}{2}g\beta H_0$ and $+\frac{1}{2}g\beta H_0$ (where $H_0$ is the external magnetic field, $\beta$ the Bohr magneton, and $g$ the spectroscopic splitting factor, the so-called "$g$-factor", which for a free electron has a value of 2.0023). When a high-frequency field is applied, transitions from one energy level to the other may occur if the condition of resonance is satisfied, *i.e.* if the energy quantum of the high-frequency field is equal to the difference between the energy levels: $h\nu = g\beta H_0$, where $h$ is Planck's constant and $\nu$ the frequency of the field (Fig. 1). In any system a larger number of electrons are present in the lower, ground level than in a higher level, and therefore more transitions will occur from the lower level: energy will be absorbed from the high-frequency field, and a resonance absorption line will be produced.

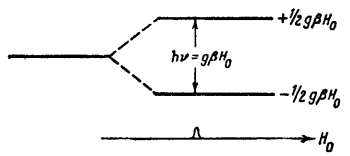



Fig. 1.

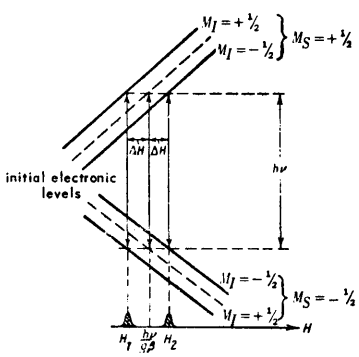



Fig. 2. Hyperfine splitting produced by coupling with one proton.

If the unpaired electron is located in a molecular orbital embracing one or more nuclei having magnetic moments, the energy levels of the electron will be split owing to interaction of the electron with these nuclei. In the particular case of interaction with one proton (nuclear spin $I = \frac{1}{2}$) two spin orientations of the proton are possible, parallel and antiparallel to the electron spin and the direction of the field; *i.e.* each electronic level is split into two. Since an electronic transition is not accompanied by a change in orientation of the nuclear spin, the selection rule is written $\Delta M_I = 0$, *i.e.* transitions will take place between states having identical components of the nuclear spin. The values of the magnetic field at which absorption of energy from the high-frequency field will occur will then be

$$H_1 = \frac{h\nu}{g\beta} - \Delta H,$$

$$H_2 = \frac{h\nu}{g\beta} + \Delta H \text{ (Fig. 2)}.$$

Thus interaction with the proton results in two lines instead of one. This is termed "hyperfine splitting", and the complex structure of the spectra is termed a "hyperfine structure". The number of components of the hyperfine structure is $2I + 1$, where $I$ is the nuclear spin. When an electron interacts with one nucleus, all components of the hyperfine structure are separated from one another by the same distance, which is termed the "hyperfine coupling constant". When an unpaired electron interacts with more than one nucleus, it is necessary to introduce several hyperfine coupling constants.

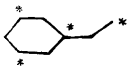
Since the hyperfine splitting is caused by interaction of the electron with the nucleus, the constant should clearly depend on the unpaired-electron density on the given nucleus. In 1956 McConnell suggested[4] that in aromatic hydrocarbon radicals there is a direct relation between the proton splitting $a_H$ and the unpaired-electron density $\rho_C$ on the carbon atom adjacent to the proton: $a_H = Q\rho_C$, where $Q$ is a constant. (The theoretical derivation of this relation and the origin of a hyperfine structure in aromatic free radicals will be discussed in Section 1.)

Subsequent work by Weissman, de Boer, and others showed that the McConnell relation is obeyed quite accurately with positive and negative ions of naphthalene[5,6], anthracene[6-8], and also many other aromatic hydrocarbon radicals. Theoretical values can be calculated for the unpaired-electron density in these compounds by the simple Hückel molecular orbital method[9]. Since, when one unpaired electron is present in a hydrocarbon radical system, the total density $\sum_{i=1}^{N} \rho_{iC}$ is unity ($N$ being the number of carbon atoms in the radical), it is evident from the above equation that the constant $Q$ is identical with the total proton splitting. The overall width of the spectrum with the ions of naphthalene and anthracene and in some other aromatic radicals is about 28 oersteds: *i.e.* the constant $Q$ has a value of 28 oersteds.

As experimental data accumulated, it became clear that by no means all the results could be explained on the basis of McConnell's hypothesis about the relation between hyperfine structure and unpaired-electron density. Thus, for example, the total proton splitting in the negative pyrene ion[6] and that in perinaphthenyl[10] are far larger than 28 oersteds (32 and 49 oersteds respectively).

Similarly, theoretical calculations of the unpaired-electron density by the Hückel method cannot explain, either

qualitatively or quantitatively, the spectra of alternant hydrocarbons containing an odd number of carbon atoms. The atoms in the molecule of an alternant hydrocarbon can, by definition, be divided into two groups, such that a member of one group, say an atom marked by an asterisk, has only atoms of the other system (without an asterisk) as neighbour:



If the molecule contains an odd number of carbon atoms, the Hückel theory predicts that the coefficients for the atomic orbitals of the atoms without asterisks are zero, and hence zero unpaired-electron densities for these atoms.

Brovetto and Ferroni[11] pointed out that hyperfine interaction may be either positive or negative, and in general, therefore, it is necessary to calculate not the unpaired-electron density but the spin density, which may be positive or negative depending on the polarisation of the $z$-component of the electron spin. In this case the total splitting of the resonance spectrum is $Q\sum_i \rho_C$, *i.e.* the sum of the moduli taking into account negative values of the spin density may be greater than unity, and therefore the splitting itself becomes greater than 28 oersteds. Negative spin densities can be obtained in the valence bond method. In particular, if all the $2n + 1$ carbon atoms in an alternant hydrocarbon are numbered from 1 to $2n + 1$, the valence bond method predicts the presence of negative spin densities at the even-numbered atoms[12,13] (the atoms without asterisks in Hückel's theory). Up to the present this method has been used to investigate the distribution of spin density in a large number of compounds: triphenylmethyl[11,14], benzyl[15], dimesitylmethyl[16], diphenylpicrylhydrazyl[17], 1- and 2-methylnaphthenyls[15], cyclopentyl and cyclohexyl[18], and the polystyrene radical[19].

In order to obtain negative spin densities by the molecular orbital method, it proved necessary to carry out the calculations not by the simple Hückel method but including the interaction of the electrons with one another. Under the influence of the unpaired electron (which has a definite spin direction), orbitals with previously balanced spins become partly uncoupled, *i.e.* an electron density appears having a spin opposite to that of the unpaired electron. In this way, owing to the different projections of the spins, the electrons have densities of opposite sign. For a detailed examination of the appropriate methods of calculating spin densities and comparing theoretical and experimental results, we must first attempt an analysis of hyperfine structure in aromatic radicals and a theoretical definition of spin density.

## 1. CONCEPT OF SPIN DENSITY

As already remarked, the cause of the complicated structure of the electron paramagnetic resonance spectra of polyatomic free radicals is the hyperfine interaction between the unpaired electron and magnetic nuclei within the molecule. To a first approximation this coupling is in effect that between the spin magnetic moments of the electron and nucleus and the electric field of the electron and the quadrupole moment of the nucleus. In free radicals, however, the latter coupling can be disregarded, since the nuclei usually investigated, $^1H$, $^{13}C$, and $^{14}N$, have either small or zero quadrupole moments.

The hyperfine coupling energy between the magnetic moments of the electron and the nucleus can be represented, in the form of a Hamiltonian, as the sum of two parts[20]:

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} \qquad (1.1)$$

(the strong magnetic field is directed along the $z$-axis), where

$$\hat{H}^{(1)} = \mu_0 \sum_{k,n} \frac{\mu_n \sigma_{zk} \sigma_{zn} (1 - 3\cos^2 \Theta_{kn})}{|\vec{r}_k - \vec{r}_n|^3}, \qquad (1.2)$$

$$\hat{H}^{(2)} = -\frac{8\pi}{3} \mu_0 \sum_{k,n} \mu_n \sigma_{zk} \sigma_{zn} \delta(\vec{r}_k - \vec{r}_n). \qquad (1.3)$$

Here $\mu_0$ is the Bohr magneton and $\mu_n$ the magnetic moment of nucleus $n$, $\sigma_{zn}$ and $\sigma_{zk}$ are Pauli operators for the $z$-component of the spin of the nucleus $n$ and the electron $k$ respectively, $\vec{r}_n$ and $\vec{r}_k$ are the radius vectors of nucleus $n$ and electron $k$, $\Theta$ is the angle between the $z$-axis and $(\vec{r}_k - \vec{r}_n)$, and $\delta$ is the Dirac delta function.

The first part $\hat{H}^{(1)}$ of this Hamiltonian represents dipole-dipole coupling of the magnetic moments, leading to a hyperfine structure dependent on the orientation of the magnetic moments of electron and nucleus in the external magnetic field. This type of hyperfine structure can be observed in single crystals. Since, however, most free radicals are studied in liquid solutions or glasses, the anisotropic splitting $\hat{H}^{(1)}$ averages out at zero owing to rapid molecular rotation, and therefore makes no contribution to the hyperfine structure[21]. Thus with free radicals the greatest interest attaches to the term $\hat{H}^{(2)}$, the so-called Fermi contact term[22], which represents isotropic splitting. It is evident from Eqn. (1.3) that the contribution made by isotropic coupling with the nucleus is proportional to $\sum_k \sigma_{zk} \delta(\vec{r}_k - \vec{r}_n)$. The mathematical probability of this quantity is termed the spin density at $\vec{r}_n$:[23]

$$\rho(\vec{r}_n) = (\Psi \left| \sum_k \sigma_{zk} \delta(\vec{r}_k - \vec{r}_n) \right| \Psi), \qquad (1.4)$$

*i.e.* it is a spin-weighted charge density. Here $\Psi$ represents the complete wave function of the paramagnetic molecule.

A convenient unit for spin density is that at the proton in a hydrogen atom in its 1*s* state. Many theoretical calculations of density are based on this unit.

Since the $\delta$-function occurs in Eqns. (1.3) and (1.4), it is clear that it will differ from zero only if the amplitude of the wave function of the molecular orbital of the unpaired electron differs from zero at the point where the given nucleus is situated. If the odd electron is located in a $\pi$ orbital, it has zero density at the nucleus, and therefore only $\sigma$-type orbitals, which have their maximum amplitude at the nucleus, can given isotropic hyperfine splitting. In aromatic free radicals the unpaired electron is in a $\pi$ orbital, while the aromatic ring lies in the nodal plane, where the odd-electron density is zero. It could therefore have been expected that the unpaired electron would not couple with the ring protons. However, this clearly contradicts experiment, which shows that a distinct hyperfine structure occurs in such compounds as the radical-ions of benzene, naphthalene, and other hydrocarbons, which contain no magnetic nuclei other than $^1H$, and therefore the hyperfine structure can arise only from the ring protons. Several writers have explained this apparent anomaly by taking into account $\pi-\sigma$ configurational interaction at the carbon atom[24-26]. Weissman[24] used molecular orbital theory to

discuss proton hyperfine splitting in an aromatic system (a detailed account of his method will be found in the book by Ingram[1]). A simpler discussion of this question is given by McConnell[25].

Let us consider, following McConnell, the C–H part of an aromatic system. Fig. 3 gives a diagrammatic representation of one of the C–H bonds (side-view). We assume that the bond is localised and consists of a hydrogen 1*s* orbital (*s*) and a carbon hybridised $sp^2$ orbital, which we shall denote by σ, directed towards it. Perpendicular to the plane of the σ bond is the $p_z$ orbital of the carbon atom, which contains the unpaired electron. The other two hybridised $sp^2$ orbitals of the carbon atom are disregarded to a first approximation, and are not shown in Fig. 3. We are thus dealing with a three-electron system in which one electron is located in the orbital *s*, another in the hybridised orbital σ, and the third in a $p_z$ orbital. The orbital part of the wave function is then written

$$\Theta(1,2,3) = p_z(1)\,\sigma(2)\,s(3), \tag{1.5}$$

and the spin–orbital configurations of the ground state

$$\begin{aligned} \Phi_1 &= A\,\Theta(1,2,3)\ \alpha\alpha\beta, \\ \Phi_2 &= A\Theta(1,2,3)\,\alpha\beta\alpha, \\ \Phi_3 &= A\Theta(1,2,3)\,\beta\alpha\alpha. \end{aligned} \tag{1.6}$$

Let us form linear combinations of these spin–orbital configurations:

$$\varphi_1 = 1/\sqrt{2}(\Phi_1 - \Phi_2), \tag{1.7}$$

$$\varphi_2 = 1/\sqrt{6}(\Phi_1 + \Phi_2 - 2\Phi_3). \tag{1.8}$$

One of the combinations $\varphi_1$ is associated with the singlet C–H state (the ground state), while the linear combination $\varphi_2$ represents an excited triplet state. The combined wave function of the ground state becomes, according to perturbation theory,

$$\varphi_1' = \varphi_1 + f\varphi_2, \tag{1.9}$$

where $f = -H_{21}/\Delta W$, $H_{21} = \langle \varphi_2 | H | \varphi_1 \rangle$, and $|f| \ll 1$, $H$ being the complete three-electron Hamiltonian.

Exact calculation shows that

$$H_{21} = -\left(\frac{\sqrt{3}}{2}\right)(J_{p\sigma} - J_{ps}), \tag{1.10}$$

where

$$J_{p\sigma} = \int p_z(i)\,\sigma(j)\,e^2/r_{ij}\,p_z(j)\,\sigma(i)\,d\tau_i\,d\tau_j, \tag{1.11}$$

$$J_{ps} = \int p_z(i)\,s(j)\,e^2/r_{ij}\,p_z(j)\,s(i)\,d\tau_i\,d\tau_j. \tag{1.12}$$

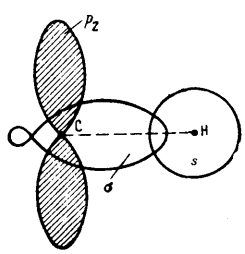



Fig. 3.

Neglecting $J_{ps}$ in comparison with $J_{p\sigma}$, we obtain

$$f = \frac{\sqrt{3}}{2}(J_{p\sigma}/\Delta W).$$

The two-electron exchange integral $J_{p\sigma}$ can be estimated from atomic spectra by the Slater method[27]. $\Delta W$ is calculated by finding the energies $W_1$ and $W_2$ corresponding to $\varphi_1$ and $\varphi_2$.

The above position corresponds to an idealised C–H bond system, in which the odd electron is entirely located in the $p_z$ orbital. In aromatic free radicals this odd electron is delocalised over the whole set of carbon atoms, *i.e.* the spin density at a C atom in this C–H system is not unity. The wave function of the ground state must then be written

$$\Psi_j = \varphi_1 + \rho_j f_j \varphi_2, \tag{1.13}$$

where $\rho$ is the spin density, while the subscript $j$ refers to the C and H atoms, and indicates that it is usually necessary to employ different $\Psi$ for different C–H bonds in the aromatic system.

Let us examine the hyperfine coupling in such a system. The energy of first-order hyperfine interaction with the proton $j$ for a doublet electronic state having spin $s = \frac{1}{2}$ is

$$\varepsilon_j(+1/2) = \langle \bar{\Psi}_j | \hat{H} | \Psi_j \rangle = 2\rho_j f_j \langle \varphi_1 | \hat{H} | \varphi_2 \rangle, \tag{1.14}$$

where $\hat{H}$ is defined by Eqn. (1.3) and

$$\varepsilon_j(+1/2) = -(\rho_j f_j/\sqrt{3})\,8\pi/3\ \mu_0\mu_I\,|s(0)|^2\,I_z.$$

Since $\epsilon_j(-\frac{1}{2}) = -\epsilon_j(+\frac{1}{2})$, $I_z = \pm\frac{1}{2}$ for the proton, and $\Delta I_z = 0$ for the electronic spin transition, the hyperfine interaction with the proton $j$ produces the splitting $a(H_j)$, which is given by

$$a(H_j) = 2/\sqrt{3}\,(\rho_j f_j)\,\frac{8\pi}{3}\,\mu_0\,\mu_I\,|s(0)|^2, \tag{1.15}$$

$$a(H_j) = 2/\sqrt{3}\,(\rho_j f_j)\ 1420\ \text{Mc/s}. \tag{1.16}$$

If we assume that $f_j$ is constant for all C–H bonds, we obtain on denoting the constants by $Q$

$$a(H_j) = Q\rho_j \quad \text{(McConnell equation)}. \tag{1.17}$$

Hence we see that from the hyperfine proton couplings we can determine the odd-electron spin densities on the carbon atoms.

The constant $Q$ was first calculated by Jarrett[28] by the valence bond method for hyperfine splitting due to one proton, on the hypothesis that the odd electron is located the whole time on one carbon atom (*i.e.* $\rho_C = 1$). The numerical value of $|Q| = 28$ oersteds showed excellent agreement with experiment. Later work by McConnell and Chesnut and the most recent investigations[12,29,30] have confirmed the proposed mechanism of hyperfine coupling, and have shown that $Q$ is negative. Physically this means that, if the resultant electron spin is parallel to the applied field, electrons in the vicinity of protons will have a spin which is antiparallel to the field; and conversely. A theoretical basis was also provided for the hypothesis of negative spin density. Let us again examine Eqn. (1.4), but for convenience determine the spin density at the point $(x, y, z)$:

$$\rho(x,y,z) = \left(\bar{\Psi}\left|\sum_k \sigma_{zk}\,\delta(r_k)\right|\Psi\right), \tag{1.18}$$

where, as previously, $\Psi$ is the complete wave function of the paramagnetic molecule. When $\Psi$ is expressed in terms

of normalised molecular orbitals $\Phi_i$, then $\rho(x, y, z)$ can be expressed as the molecular-orbital density matrix $\rho_{ij} \equiv \bar{\rho}$:

$$\rho(x, y, z) = \sum_{ij} \bar{\rho}_{ij} \Phi_j^* \Phi_i. \quad (1.19)$$

If $\Psi$ is given in terms of a set of atomic orbitals, which have not necessarily been normalised, the atomic-orbital density matrix $\rho_{\lambda\mu} \equiv \rho$ can be determined

$$\rho(x, y, z) = \sum_{\lambda,\mu} \rho_{\lambda\mu} \Phi_\mu^* \Phi_\lambda, \quad (1.20)$$

where $\Phi\mu$ and $\Phi\lambda$ are atomic orbitals. When the molecular orbitals $\Phi_i$ are expressed as linear combinations of atomic orbitals (LCAO):

$$\Phi_i = \sum_\lambda a_{\lambda i} \Phi_\lambda, \quad (1.21)$$

the matrices $\rho$ and $\bar{\rho}$ can be correlated with one another:

$$\rho_{\lambda\mu} = \sum_{i,j} \bar{\rho}_{ij} a_{\mu j}^* a_{\lambda i}. \quad (1.22)$$

In the simple molecular orbital theory disregarding electron correlation, when the complete wave function is written as one configuration, all the non-diagonal terms $\bar{\rho}ij$ are zero, while all diagonal terms are positive. Thus the spin density function is everywhere positive. The diagonal elements $\rho_{\lambda\mu}$ are in this case positive, but the non-diagonal elements may be negative. However, this does not mean that the density is negative at this point, since $(\rho_{\lambda\mu}\sigma_{\mu\lambda} + \rho_{\mu\lambda}\sigma_{\lambda\mu})$, where $\sigma_{\lambda\mu} = <\Phi_\lambda\Phi_\mu>$ is the overlap, defines the total spin between the atoms, and cannot be ascribed to only one of the neighbouring atoms.

A description by the simple molecular orbital method of a free radical having $(2k + 1)$ electrons shows that each orbital, in conformity with the Pauli principle, is occupied by not more than two electrons. The lower orbitals are occupied in pairs, while the odd electron occupies one of the lower orbitals remaining free or a higher orbital. Electrons having different spins in the same orbital interact with one another. This phenomenon (the correlation effect) may be taken into account by writing the wave function of the system in terms of molecular orbitals including different configurations. As a result of the introduction of correlation interaction, the $\bar{\rho}ij$ matrix is now non-diagonal, and any of its elements (diagonal or non-diagonal) can be zero. Moreover, in the $\rho_{\mu\lambda}$ matrix the diagonal elements can be negative, which means that the spin density function $\rho(x, y, z)$ can be negative at the given atom. Spin densities have been calculated by the molecular orbital method with configurational interaction for allyl[31,32] and the negative pyrene ion[33].

Below we shall examine other ways of describing free radicals which similarly yield states having negative spin density at the carbon atoms.

## 2. SPIN DENSITY IN THE SIMPLE HÜCKEL MOLECULAR ORBITAL THEORY

In Hückel's molecular orbital method (the simple LCAO–MO method) charge densities at any atom in a system can be calculated by means of the atomic orbital coefficients according to the relation[9]

$$q_i = \sum_j n_j c_{ij}^2, \quad (2.1)$$

where $nj$ is a number (0, 1, or 2) representing the extent to which the orbital is occupied, and $c_{ij}$ are coefficients of the atomic orbital $i$ in the molecular orbital $j$.

As already noted in the Introduction, the charge density is not in general identical with the spin density. In some regions, where there is a high charge density, the spins may be paired, and thus the spin density may be zero. If, however, the projection of the spin on a fixed axis $z$ does not vanish, for some free radicals the spin densities are, to the simple LCAO–MO approximation, proportional to the squares of the Hückel coefficients in the orbital of the odd electron. In this case Eqn. (2.1) is in fact identical with Eqn. (1.22).

Use of this simple molecular orbital theory to find spin densities and calculate hyperfine structural constants gave surprisingly good agreement with experiment for several positive and negative radical-ions of alternant hydrocarbons containing even numbers of carbon atoms. As indicated above, this theory proved valid for naphthalene[5,6] and anthracene[6–8], and also for naphthacene[8], biphenyl[7], perylene[8,34,35], $\alpha$-methylstyrene[36], pentaphenylcyclopentadienyl[37], and for compounds containing heteroatoms — the tetracyanoethylene anion[38], the cation of $p$-phenylenediamine[39], the ions of semiquinones[40–42], and for several metal ketyls[43].

The spin density was determined experimentally from the hyperfine structure of the spectra by means of McConnell's equation $a_H = Q\rho_C$. The constant $Q$ is usually given the empirical value -22.5 oersteds, obtained from the spectrum of the benzene minus ion, although the theoretical value of -28 oersteds is sometimes used.

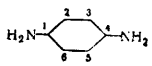
McConnell's equation has been derived to determine spin densities from hyperfine proton splitting in aromatic rings. But the protons of amino- and methyl groups also often contribute to the hyperfine structure. Bersohn[40] investigated several ions of methylated semiquinones by the molecular orbital method, and calculated the spin densities on the protons of the methyl groups, taking into account the delocalisation of the odd electron in these groups. Comparison of his calculated spin densities with experimental values in various quinones gives $Q$ - 25 oersteds. McLachlan[44] showed that, in the case of methylated semiquinones and for the hyperfine couplings of amino-group protons, we can use an equation analogous to $a_H = Q\rho$, but with $Q$ = -28 oersteds for the ring protons and $Q$ = +25 oersteds for protons of methyl or amino-groups, $\rho$ denoting in the latter case the density at the nitrogen nucleus. This agrees with Bersohn's calculations[40].

Bolton and Carrington[45] used the molecular orbital theory to explain the hyperfine structure in the spectra of the anions of toluene and $p$- and $m$-xylenes. The methyl group was regarded as an electropositive substituent, exerting an inductive effect on the aromatic ring carbon atom to which it was linked. The form selected for the Coulomb integral of such a carbon atom was $\alpha$ - 0.13$\beta$, where $\alpha$ is the Coulomb integral for all the other carbon atoms in the ring and $\beta$ is the resonance integral of the C–C bond. Values of the hyperfine coupling constants of

the ring protons, calculated from the McConnell equation with $Q$ = 22.5 oersteds, gave good agreement with experiment.

For the hyperfine splitting due to the fluorine nuclei in fluorinated semiquinones Anderson *et al.*[46] derived the relation $a_F = -39.3\rho_C$, where $\rho_C$ is the density at the carbon atom adjacent to the fluorine atom. The equation was obtained on the assumption that the configurational interaction in the ·(C–F) bond is the same as in the ·(C–H) bond and that $\rho_C$, the total spin density, is the same in the tetrahydrosemiquinones and the fluorosemiquinones. Confirmation of the correctness of this relation was provided by a recent study of the negative ion of *p*-fluoronitrobenzene[47]. The results differed only by 20% from those of the previous paper. Agreement is obtained with experiment when $Q$ = = -47.5 oersteds.

As an example of the use of the basic equation with different values of $Q$, let us consider in greater detail the positive ion of *p*-phenylenediamine[39]:



The observed electron paramagnetic resonance spectrum gives the following values for the isotropic hyperfine coupling constants:

$$a_N = 5.29 \text{ oersteds},$$
$$a_H(NH_2) = 5.8 \text{ oersteds},$$
$$a_H(\text{ring}) = 2.13 \text{ oersteds}.$$

The McConnell equation (with $Q$ = 28 oersteds) gave spin densities of $\rho_C = 0.07$ at the carbon atoms numbered 2, 3, 5, and 6. A simple calculation was made of the molecule by the LCAO–MO method, in which all the resonance integrals $\beta$ were taken as equal, while the Coulomb integral for the nitrogen atom $\alpha_N$ was represented by a parameter defined in such a way that it corresponded to the value found for $\rho_C$. This value was $\alpha_N = \alpha_C + 0.85\beta$, where $\alpha_C$ is the Coulomb integral for the carbon atom. Using this parameter, the odd-electron density in the $p_z$ orbital of the nitrogen atom was calculated to be $\rho_N = 0.236$. If $Q$ is taken as -25 oersteds, we obtain from the equation $a_H(NH_2)$ = = -5.9 oersteds, in excellent agreement with the constant obtained empirically.

It is more difficult to explain the isotropic hyperfine coupling at the $^{14}N$ nitrogen nucleus. In the paper under consideration hypotheses were put forward as to possible mechanisms for the formation of the hyperfine structure. Such a structure requires the presence of odd-electron density in a 2*s* orbital at the N nucleus. Transfer of odd-electron density to the σ system, and thus to a 2*s* orbital at the nitrogen atom, can, in the opinion of these authors, take place in two ways: (1) by π–σ coupling at the neighbouring carbon atom, transferring spin density to the C–N bond, or (2) by π–σ coupling at the nitrogen atom, transferring the spin density to all three σ bonds of the nitrogen. The ratio $a_N/a_H(NH_2)$ can be calculated on the assumption that the second mechanism is responsible both for the hyperfine splitting due to the nitrogen nucleus and for the splitting caused by protons in the amino-groups:

$$\frac{a_N}{a_H} = 0.0723\frac{|\varphi_N(0)|^2}{|\varphi_H(0)|^2} \qquad (2.2)$$

It is postulated that the ion has a planar configuration and $sp^2$ hybridisation at the nitrogen atom. The three hybrid σ orbitals are approximately orthogonal linear combinations of the atomic orbitals $(2s)_N$, $(2p_x)_N$, and $(2p_y)_N$. Assuming the (N–H) bond to be non-polar, we write it as

$$\psi_\sigma = \frac{1}{\sqrt{2}(1+\Delta)^{1/2}}\{(sp^2)_N + (1s)_H\}, \qquad (2.3)$$

where Δ is the overlap integral. Remembering that the main contribution at the nitrogen nucleus is made by the 2*s* function, we write

$$\frac{a_N}{a_H} = -0.0723\frac{|2s_N(0)|^2}{|1s_H(0)|^2}. \qquad (2.4)$$

The negative sign arises from the fact that a particular polarisation of electron spin at the nitrogen nucleus produces a polarisation of opposite sign at the proton[48].

Estimating $|2s_N(0)|^2$ by the Hartree–Fock method and $|1s_H(0)|^2$ from the Schrödinger function $(\pi a_0^3)^{-1}$, we have

$$|2s_N(0)|^2 = 33.4 \times 10^{24} \text{ cm}^{-3}, \qquad (2.5)$$
$$|1s_H(0)|^2 = 2.15 \times 10^{24} \text{ cm}^{-3},$$
$$a_N/a_H = -1.12. \qquad (2.6)$$

Experiment gives 0.9. Thus in this ion mechanism (2) does actually provide the main proportion of the hyperfine splitting due to the nitrogen nucleus. For this splitting we can then use an expression of the McConnell type, where the quantity $Q_N$ = 22.4 oersteds satisfies the experimental data when the simple molecular orbital theory is applied. However, the mechanism of hyperfine coupling at the nitrogen nucleus is far more complicated. As Karplus and Fraenkel[49] have recently shown, a complete discussion of the splitting due to the nitrogen atom requires consideration of the effect not only of 2*s* but also of 1*s* electrons (see Section 3, below).

Hyperfine splitting due to the nitrogen nucleus and spin densities have been computed empirically also in phenazine semiquinone (spin density at the nitrogen nuclei of the NH groups $\rho_N$ = -0.256) and in other semiquinones containing nitrogen[50,51]. Bersohn[52] made a theoretical calculation of spin densities at the nitrogen atoms in diphenylpicrylhydrazyl by the simple LCAO–MO method. The estimated spin densities at the two central nitrogen atoms were $\rho_1$ = = 0.1416 and $\rho_2$ = 0.1518. Holmberg *et al.*[53] calculated spin densities using experimental data on isotropic and anisotropic hyperfine splitting in diphenylpicrylhydrazyl, and obtained values of $\rho_1$ = 0.274 and $\rho_2$ = 0.605 (or 0.396). Two values are given for $\rho_2$ because of uncertainty in the choice of the hyperfine coupling tensor.

## 3. HYPERFINE SPLITTING DUE TO THE $^{13}C$ NUCLEUS

Several papers have dealt with the distribution of spin density in hydrocarbons in which a considerable proportion of the $^{12}C$ atoms have been replaced by the $^{13}C$ isotope, which has non-zero spin, and which can therefore yield information on the spin density in a molecule not only from the proton splitting but also from that caused by the $^{13}C$ nucleus.

Tuttle[54] suggested for the spin distribution in the negative naphthalene ion containing $^{13}C$ atoms the empirical equation

$$a_i = k_i\rho_i + \sum_j k_{ij}\rho_j, \qquad (3.1)$$

where $a_i$ is the hyperfine splitting in position $i$ due to $^{13}C$, $\rho_i$ the density of the unpaired $\pi$ electron in this position, and $\rho_j$ the unpaired $\pi$ electron density at the neighbouring carbon atoms.

Reitz *et al.*[55] used this equation to determine spin densities in semiquinones by means of the $^{13}C$ splitting. The value of $k_i$ is known for the proton splitting $k_{C-H}$ (*i.e.* $Q$ in the McConnell equation), while values of $k_{C-C}$ were taken from Tuttle's calculations for $^{13}C$ splitting in the $\alpha$- and $\beta$-positions in the negative naphthalene ion. The results show good agreement with Bersohn's calculations[40]:



| Spin density according to Bersohn | Spin density according to Reitz |
|---|---|
| $\rho_0=0.206$ | $\rho_0=0.221$ |
| $\rho_1=0.090$ | $\rho_1=0.078$ |
| $\rho_2=0.113$ | $\rho_2=0.123$ |

The spin density at the $^{13}C$ nucleus was determined in benzonitrile[56] in which 64% of the carbon atoms in the nitrile group had been replaced by the isotope. The $^{13}C$ splitting was 6.4 oersteds, and the spin density at the $^{13}C$ carbon nucleus was 0.051 compared with the hydrogen atom in the 1*s* state.

In triphenylmethyl[6], in which the methyl carbon had been replaced by $^{13}C$, the splitting in liquid solution was 26 oersteds, the corresponding spin density at the $^{13}C$ nucleus being $\rho_{^{13}C} = 0.22$. Similarly, we can determine the spin density at the protons (from the total proton splitting of 35 oersteds) as $\rho_H = 0.068$ and the total density at the carbon atoms numbered 2, 3, 4, 5, and 6 as $\rho_C = 1.57$.[57] The value of $\rho_{^{13}C}$ calculated from the McConnell equation, with $Q$ taken as the isotropic splitting in the negative naphthalene ion, is 0.68, which is close to the spin density calculated theoretically (for one of the configurations of triphenylmethyl the valence bond method[57] gives $\rho_{^{13}C} = 0.616$).

The empirical equation (3.1) has received theoretical justification[30]. The hyperfine coupling constant for a $^{13}C$ nucleus linked to three other carbon atoms was found to be represented by the relation

$$A_C = Q_1\rho_0^\pi + Q_2(\rho_1^\pi + \rho_2^\pi + \rho_3^\pi), \qquad (3.2)$$

where $\rho_0^\pi$ is the spin density at the atom having the $^{13}C$ nucleus, $\rho_1^\pi$, $\rho_2^\pi$, and $\rho_3^\pi$ are the spin densities at the adjacent carbon atoms, and the $Q$ are $\pi-\sigma$ configurational interaction constants. This equation was used to determine the hyperfine structural constants in the negative naphthalene ion having the natural content of the $^{13}C$ isotope[58]. The agreement with experiment is quite good, but some discrepancies are inevitable, since some quite crude assumptions were made in deriving Eqn. (3.2).

Ward[59] used this equation to determine the constants $Q_1$ and $Q_2$ in the negative bipyridyl ion. Spin densities at the nitrogen and carbon atoms were calculated by Hückel's molecular orbital method, the resonance integrals being put equal for all the bonds, while the Coulomb integral for the nitrogen atom was chosen as $\alpha_N = \alpha_C + \beta h$, where $\alpha_C$ is the Coulomb integral for the carbon atom, $\beta$ the resonance integral, and $h$ a parameter which is adjusted to give the best agreement with experiment. When $h = 0$, the spin densities in the negative bipyridyl ion coincide with those in the biphenyl ion. The simple LCAO–MO method then leads to values of $\rho_N = 0.159$, $\rho_o = 0.019$, $\rho_m = 0.089$, and $\rho_p = 0.123$ for the spin densities at the nitrogen atom and in the *ortho-*, *meta-*, and *para*-positions respectively. The experimental values of $\rho_o$ and $\rho_m$ are 0.02 and 0.10 respectively. Application of Eqn. (3.2) to these spin densities and the experimental splitting due to the nitrogen nucleus yields $Q_1 = 19$ and $Q_2 = 9.5$ oersteds. With these values of $Q$ the Hückel theory can be used to estimate the hyperfine coupling constants in other nitrogen-containing ions. In particular, Ward's estimate of the hyperfine splitting due to the nitrogen atom in the negative phenazine ion agreed well with experiment.

However, Eqn. (3.2) does not always yield results agreeing with experiment. In order to examine hyperfine splitting due to $^{13}C$ (or $^{14}N$) nuclei, the effect of the inner, coupled 1*s* electrons must be taken into account[49]. The 2*s* and 2*p* electrons are involved in the formation of molecular orbitals extending throughout the molecule. It is supposed that the contribution of the 1*s* electrons to the hyperfine coupling arises primarily from their transition to antibonding molecular orbitals. For the lowest doublet state of the carbon atom in the $CH_3$ radical, for example, the wave function is written as a determinant of the form

$$\Psi_0 = (9!)^{-1/2}|\,1s(1)\alpha(1)\,1s(2)\beta(2)\,\sigma_1(3)\alpha(3)\,\sigma_1(4)\beta(4)\times \times\sigma_2(5)\alpha(5)\,\sigma_2(6)\beta(6)\,\sigma_3(7)\alpha(7)\,\sigma_3(8)\beta(8)\,\pi(9)\alpha(9)|, \qquad (3.3)$$

where 1*s* and $\pi$ represent 1*s* and $\pi$ orbitals of the carbon atom, while the $\sigma_i$ ($i$ = 1, 2, 3) represent bonding molecular orbitals of the type

$$\sigma_i = N\{3^{-1/2}[(2s + \sqrt{2}(2p\sigma_i)] + \ldots\}. \qquad (3.4)$$

Here the $2p\sigma_i$ orbitals are directed along the $\sigma_i$ bond, the leader denoting orbitals of the neighbouring atoms. They need not be discussed in detail, since they do not overlap the 1*s* orbitals.

After transfer of a 1*s* electron to the antibonding molecular orbital

$$\sigma_i^* = N\{3^{-1/2}[(2s) + \sqrt{2}(2p\sigma_i)] - \ldots\},$$

the excited state is written

$$\Psi_i = (9!)^{-1/2}|\,\sigma_i^*(1)\alpha(1)\,1s(2)\beta(2)\,\sigma_1(3)\alpha(3)\ldots\sigma_3(8)\beta(8)\,\pi(9)\alpha(9)|\,. \qquad (3.5)$$

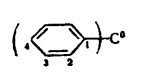
The contribution of the 1*s* electrons to the spin density at the nucleus, which is proportional to that at the atom containing the nucleus, can then be determined exactly by means of perturbation theory. This contribution can be written $S^C\rho^\pi$, and from the atomic model for $CH_3$, we have $S^C = -12.7$ oersteds.

The final expression obtained by Karplus and Fraenkel[49] for the hyperfine splitting due to the $^{13}C$ nucleus in an atom linked to three other atoms $X_1$, $X_2$, $X_3$ ($sp^2$ hybridisation) is of the form

$$a^C = \left(S^C + \sum_{i=1}^{3} Q^C_{CX_i}\right)\rho^\pi + \sum_{i=1}^{3} Q^C_{X_iC}\rho_i^\pi, \qquad (3.6)$$

where $\rho^\pi$ is the spin density at the carbon atom and $\rho_i^\pi$ the spin density at the atom $X_i$. The contribution of the 1*s* electrons is determined by the value of $S^C$, while those of the 2*s* electrons are determined by $Q^C_{CX_i}$ and $Q^C_{X_iC}$, the former $Q$ determining the hyperfine splitting due to the nucleus of the carbon atom C and the transfer of spin density to the $CX_i$ bond, while $Q^C_{X_iC}$ governs the contribution

TABLE 1.

| Radical | Position of atom | Spin density $\rho_i^\pi$ | Value of $a_i^C$ | |
|---|---|---|---|---|
| | | | calc. | expt. |
| Methyl | | 1.000 | 43.8 | ±41±3 |
| $\overset{2}{\underset{1}{(HOOC)_2}}\overset{0}{CH}$ | 0 | 0.892 | 31.8 | 33.0 |
| | 1 | 0.0 | −12.4 | |
| (radical of malonic acid) | 2 | 0.05 | | |
| Negative naphthalene ion | α | 0.2087 | 7.38 | ±7.1 |
| | β | 0.0786 | −1.20 | ±1.2 |
| | γ | −0.0746 | −7.06 | |
| Negative benzene ion | | 0.1667 | 1.30 | ±2.4 |
| Negative cyclooctatetraene ion | | 0.1250 | 0.97 | ±1.3 |
| Triphenylmethyl | 0 | 0.68 | 26.2 | 26 |
| | 1 | −0.1299 | | |
|  | 2 | 0.1067 | | |
| | 3 | −0.0468 | | |
| | 4 | 0.1168 | | |

to the hyperfine splitting of the spin densities at the atoms $X_i$ and the transfer of spin density to the $X_iC$ bond. These contributions are of opposite signs.

It is evident from Eqn. (3.6) that knowledge of the $\pi-\sigma$ interaction parameters ($Q$ and $S^C$) and of the $\pi$-electron spin densities $\rho_i^\pi$ is necessary in order to estimate theoretically the hyperfine splitting due to the $^{13}C$ (or $^{14}N$) nucleus. Karplus and Fraenkel obtained theoretical values (in oersteds) for the $CHC_2$ radical of $S^C = -12.7$, $Q^C_{CH} = 19.5$, $Q^C_{CC'} = 14.4$, and $Q^C_{C'C} = -13.9$.

These quantities, together with values of $\rho_i^\pi$ obtained either by the Hückel method or from the proton splitting by means of the McConnell equation, have been used to determine the constants $a^C$ for the methyl radical, the radical of malonic acid, the negative ions of naphthalene, benzene, and cyclooctatetraene, the ion of $p$-benzosemiquinone, and triphenylmethyl. In calculating spin densities by means of the McConnell equation, a value of -23.72 oersteds was used for the $\pi-\sigma$ configurational interaction constant $Q^H_{CH}$. This value was obtained by examining the contribution of 2$s$ electrons to the $^{13}C$ splitting by the valence bond method.

Table 1 compares the experimental constants $a^C$ with values calculated by means of Eqn. (3.6). It is seen that the two results are in excellent agreement.

## 4. SPIN DENSITY IN THE SELF-CONSISTENT FIELD METHOD

McLachlan[60] has recently shown that the self-consistent field theory may give the best values for the spin density in both alternant and non-alternant $\pi$-electron radicals. The wave function in radicals is usually written as a determinant:

$$\chi_0 = \| \psi_1^\alpha \psi_2^\beta \ldots \psi_n^\beta \psi_0^\alpha \|, \qquad (4.1)$$

in which the $2n$ electrons occupy the $\Psi_n$ orbitals in pairs, while the odd electron with spin $\alpha$ occupies the orbital $\Psi_0$. This function is not self-consistent in the full sense, since, in contrast to self-consistent wave functions, it can combine with excited doublet configurations $\chi_i^r$:

$$\chi_i^r = \| \psi_1^\alpha \ldots \psi_r \psi_n^\beta \psi_0 \| \frac{1}{\sqrt{6}} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha). \qquad (4.2)$$

where one electron from the orbital $i$ passes to the vacant orbital $r$. The matrix element between these states is the exchange integral

$$\langle \chi_0 \hat{H} | \chi_i^r \rangle = -\frac{3}{\sqrt{6}} \iint \psi_0^* \psi_r(1) \frac{e^2}{r_{12}} \psi_i^* \psi_0(2)\, d\tau_1\, d\tau_2. \qquad (4.3)$$

Some workers have suggested using a different form of wave function in radicals. Hoijtink[61] took as the function for the ground state

$$\Psi = \chi_0 + \sum_{i,r} \lambda_{ir} \chi_i^r, \qquad (4.4)$$

instead of $\chi_0$, and regarded the exchange energy as a small perturbation. But, as McLachlan points out, here the calculations are complicated, especially with large molecules, where there are many excited configurations.

Pople and Nesbet[62] suggested a self-consistent wave function of the type

$$\Phi = \| \psi_1^\alpha \psi_1'^\beta \ldots, \psi_n^\alpha \psi_n'^\beta \psi_0^\alpha \|, \qquad (4.5)$$

in which electrons with spins $\alpha$ and $\beta$ occupy independent sets of orbitals $\Psi_0$, $\Psi_1$, ..., $\Psi_n$; $\Psi_1'$, ..., $\Psi_n'$.

The spin densities in the Pople–Nesbet function

$$\rho = |\psi_0|^2 + \sum_i \{|\psi_i|^2 - |\psi_i'|^2\}, \qquad (4.6)$$

may be negative at the nodes of $\Psi_0$ if $|\Psi_i'|^2$ exceeds $|\Psi_i|^2$.

The spin density may be negative also in the Hoijtink function

$$\rho = \rho_0 + 2 \sum_{i,r} \lambda_{ir} \langle \chi_0 | \rho | \chi_i^r \rangle. \qquad (4.7)$$

In the case of radical-ions McLachlan suggested applying Pariser and Parr's semiempirical method[63] to the Pople–Nesbet function. The LCAO–MO coefficients for the two sets of orbitals

$$\psi_0 = C_{0r}\Phi_r, \quad \psi_i = C_{ir}\Phi_r; \quad \psi_i' = C_{ir}'\Phi_r, \qquad (4.8)$$

are then defined by the equations

$$\left.\begin{aligned} \sum_s F_{rs} C_{is} &= E_i C_{ir} \\ \sum_s F_{rs}' C_{is}'' &= E_i' C_{ir} \end{aligned}\right\} \quad s = 1 \ldots\ldots 2n+1, \qquad (4.9)$$

$$\sum_s F_{rs} C_{0s} = E_0 C_{0r} \qquad \sum_s F_{rs}^0 C_{0s} = E_0 C_0 .$$

The quantities $F$, $F'$, and $F^0$ represent the self-consistent field for electrons having spins $\alpha$ and $\beta$ and for the odd electron, and they depend on the bond orders and electron densities for the electrons with spins $\alpha$ and $\beta$, which are defined as

$$P_{rs} = \sum_{i=1}^{n} C_{ir} C_{is} \quad P_{rs}' = \sum_{i=1}^{n} C_{ir}' C_{is}' \quad P_{rs}^0 = C_{0r} C_{0s}. \qquad (4.10)$$

The operators $F$ and $F'$ can then each be written as a sum of three terms:

$$F = V + K - J, \qquad (4.11)$$

$$F' = V + K - J', \qquad (4.12)$$

where $V$ is the field of the nucleus and the $\sigma$ electrons, $K$ the Coulomb field of all the $\pi$ electrons, $J$ and $J'$ represent the exchange field for $\pi$ electrons having spins $\alpha$ and $\beta$,

and $F^0$ is the field due to all the electrons other than the odd electron; $F^0$ is obtained from $F$ by omitting terms proportional to $P^0$:

$$V_{rs} = \beta_{rs} - \delta_{rs} \sum_{t \neq r} \gamma_{rt}, \quad (4.13)$$

$$K_{rs} = \delta_{rs} \sum_{t} (P_{tt} + P'_{tt} + P^0_{tt}) \gamma_{rt}, \quad (4.14)$$

$$J_{rs} = (P_{rs} + P^0_{rs}) \gamma_{rs}, \quad (4.15)$$

$$J' = P_{rs} \gamma_{rs}. \quad (4.16)$$

Hence it can be seen that the difference between $F$ and $F'$ arises from the exchange field $J - J'$ of the odd electron. In Eqn. (4.13) the resonance integral $\beta_{rs}$ is a non-diagonal matrix element, which is zero for atoms $r$ and $s$ not directly linked to one another and has the value $\beta$ for all C–C bonds; the Coulomb integral $\beta_{rr}$ is a diagonal matrix element with respect to the one-electron integral containing the kinetic energy; and $\gamma_{rs}$ is the Coulomb electrostatic coupling of the electrons in $\Phi_r$ and $\Phi_s$.

With neutral radicals the spin density can be estimated by the molecular orbital method taking into account perturbation theory. Self-consistent orbitals are taken as the starting point, while the exchange interaction of the odd electron with other, coupled electrons is regarded as a perturbation. If the unperturbed molecule is alternant, $P_{rr} = P'_{rr} = \frac{1}{2}$. Furthermore $P_{rs} = P'_{rs}$, and these vanish if the atoms $r$ and $s$ belong to the same set. The operator $F$ is then

$$F(0)_{rr} = \beta_{rr} + 1/2 \gamma_{rr}, \quad (4.17)$$

$$F(0)_{rs} = \beta_{rs} - P(0)_{rs} \gamma_{rs}. \quad (4.18)$$

The first correction to $F(0)$ is given by $F^0(1)_{rs} = F^0(0)_{rs}$.

$$K(1)_{rs} - K(0)_{rs} = \sum_{t} P^0(0)_{tt} \gamma_{rt} \delta_{rs}, \quad (4.19)$$

$$J(1)_{rs} - J(0)_{rs} = P^0(0)_{rs} \gamma_{rs} = G_{rs}, \quad (4.20)$$

$$F^0(1)_{rs} = F^0(0)_{rs}. \quad (4.21)$$

Here $G_{rs}$ is the exchange potential of the odd electron. Even to this first approximation the orbital of the odd electron and the total electron density are found not to vary, while the change in spin density is caused entirely by the exchange term $G_{rs}$. The exchange potential $G$ of the odd electron affects the spin density by changing the effective values of the Coulomb integrals $\alpha_r$ and the resonance integrals $\beta_{rs}$ for electrons having a spin $\alpha$. The method of Coulson and Longuet-Higgins[64], which takes into account the coefficients of mutual polarisability $\pi_{rs,tu}$, gives for the perturbed spin density

$$\rho_{rs} = \rho(0)_{rs} - \frac{1}{2} \sum_{t,u} \pi_{rs,tu} G_{tu}. \quad (4.22)$$

Equating the $\gamma_{rr}$ and replacing $\pi_{rs,tu}$ by $\pi_{rs}$ (since the polarisabilities of the atomic bonds are zero if $t$ and $u$ are located in different systems), we have

$$\rho_r = C^2_{0r} - \frac{1}{2} \gamma \sum_{s} \pi_{rs} C^2_{0s}, \quad (4.23)$$

where $\pi_{rs}$ is the mutual polarisability of the two atoms. It is calculated from the expression

$$\pi_{rs} = -4 \sum_{i} \sum_{j} \frac{C_{ri} C_{sj} C_{si} C_{rj}}{E_j - E_i}, \quad (4.24)$$

where $i$ and $j$ are occupied and vacant orbitals, and $E_i$ is the energy of the Hartree–Fock parameters.

From a comparison of the results obtained for spin density calculated by means of self-consistent orbitals and the Hückel orbitals used in Eqn. (4.23), McLachlan concludes that the latter can give almost the same result as the former if the right value is chosen for the resonance integral.

According to the self-consistent field theory, the resonance integral is given by

$$\beta_{rs(\mathrm{eff})} = \beta_{rs} - \frac{1}{2} P_{rs} \gamma_{rs}, \quad (4.25)$$

where $P_{rs}$ is the overall bond order. Using the Pariser and Parr parameters $\gamma = 10.53$ eV, $\beta_{12} = -2.39$ eV, $\gamma_{12} = 7.30$ eV, and $\beta$ about -4.5 in most cases, we obtain

$$1/2 \gamma/\beta \simeq -1.2 = -\lambda. \quad (4.26)$$

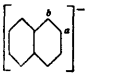
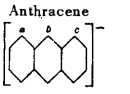
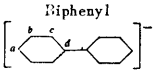
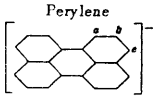
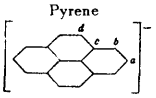
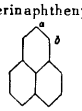
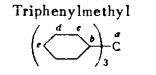
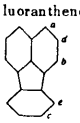
Thus we can replace (4.23) by

$$\rho_r = C^2_{0r} - \lambda \sum_{s} \pi_{rs} C^2_{0s}, \quad (4.27)$$

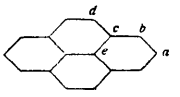
where $\pi_{rs}$ is a numerical quantity, and the only parameter which must be aribtrarily chosen is $\lambda$.

McLachlan calculated the hyperfine structural constants on the assumption that each constant depends not only on $Q$ but also on $\lambda$. The latter varies only slightly on passing from one compound to another, while $Q$ is constant, its value being -24.2 oersteds. Although the simple Hückel theory proved successful for many hydrocarbons, the spectrum of the negative pyrene ion can be explained only by

TABLE 2.

| Free radical | Spin densities | | |
|---|---|---|---|
| | expt. | Hückel method | Hartree – Fock method |
| Naphthalene  | *a* 0.076<br>*b* 0.203 | 0.069<br>0.181 | 0.055<br>0.211 |
| Anthracene  | *a* 0.230<br>*b* 0.113<br>*c* 0.064 | 0.193<br>0.096<br>0.048 | 0.256<br>0.118<br>0.032 |
| Biphenyl  | *a* 0.227<br>*b* 0.019<br>*c* 0.113<br>*d* 0.085 | 0.159<br>0.019<br>0.089<br>0.123 | 0.208<br>—0.023<br>0.105<br>0.128 |
| Perylene  | *a* 0.128<br>*b* 0.019<br>*c* 0.146 | 0.083<br>0.013<br>0.108 | 0.115<br>—0.031<br>0.145 |
| Pyrene  | *a* 0.054<br>*b* 0.240<br>*d* 0.054 | | —0.052<br>0.187<br>0.092 |
| Perinaphthenyl  | *a* 0.038<br>*b* 0.327 | | —0.098<br>0.247 |
| Triphenylmethyl  | *a* 0.68<br>*c* 0.124<br>*d* 0.062<br>*e* 0.124 | | 0.516<br>0.101<br>—0.041<br>0.087 |
| Fluoranthene  | *a* 0.215<br>*b* 0.161<br>*c* 0.054<br>*d* 0.000 | | 0.227<br>0.157<br>0.037<br>—0.023 |

means of the self-consistent field theory. On the Hückel theory the orbital of the odd electron has nodes at atoms *a* and *e*, and hyperfine splitting should be caused by the protons in positions *b* and *d*:




The spectrum should then consist of 25 lines. Experiment gives 75 lines, which indicates the presence of considerable spin density at position *a*. The self-consistent field method predicts the presence of negative spin density at this position, and gives a good numerical estimate.

Non-alternant ions as well as alternant radical-ions were studied in this work. In the former the electronic states are not coupled as in the alternant type, and this affects to some extent the calculations of spin density, although for simplicity the equations derived for alternant ions were utilised. The negative acenaphthylene ion, the negative fluoranthene ion, and the positive and negative acepleiadylene ions were investigated. The spectra of the two acepleiadylene ions are quite different, and for them neither the Hückel theory nor the self-consistent field theory agrees with experiment. Spin density was calculated also for the neutral radicals triphenylmethyl, perinaphthenyl, allyl, and benzyl. Table 2 compares experimental and theoretical values of spin densities calculated by the Hückel molecular orbital method and by the self-consistent field method.

## 5. SPIN DENSITY IN ALIPHATIC RADICALS

In contrast to aromatic free radicals, comparatively little study has been made of aliphatic free radicals by electron paramagnetic resonance, and hardly any work has been done on the theoretical determination of their spin density distributions. The difficulty in investigating aliphatic radicals is that they are usually obtained either during irradiation or by being trapped in solids, and it is often difficult to identify the spectrum of the resulting radical, since rupture of bonds may take place at different points. Sometimes anisotropy must also be taken into account, since most work on aliphatic radicals is not done in solution.

Whereas in aromatic free radicals the total extent of the spectrum is independent of the number of protons involved in hyperfine coupling, for aliphatic radicals the total width of the spectrum is sensitive to the number of protons.

Chesnut[65] gave a molecular orbital treatment of aliphatic radicals, the ethyl, isopropyl, and t-butyl radicals being considered. Hyperfine coupling in these radicals can be explained by means of the theory of hyperconjugation[66,67] which, although a very crude approximation, nevertheless gives comparatively good qualitative agreement with experiment.

It is supposed that combinations of the atomic orbitals of hydrogen form hydrogen group orbitals of the type

$$\chi_1 = \frac{\Phi_1 + \Phi_2 + \Phi_3}{(3 + 6S_{HH})^{1/2}}, \qquad (5.1)$$

$$\chi_2 = \frac{2\Phi_1 - \Phi_2 - \Phi_3}{(6 - 6S_{HH})^{1/2}}, \qquad (5.2)$$

$$\chi_3 = \frac{\Phi_2 - \Phi_3}{(2 - 2S_{HH})^{1/2}}. \qquad (5.3)$$

If the wave functions of the methyl carbon atom [in the ethyl radical (Ed. of Translation)] are denoted by $sp_1$, $p_2$, and $p_3$, the one of the hybridised $sp_1$ orbitals forms a $\sigma$ bond with $\chi_1$, while the $p_2$ and $p_3$ orbitals form bonds of $\pi$ type with $\chi_2$ and $\chi_3$ respectively. The second carbon atomic $sp_1$ orbital is utilised for a $\sigma$ bond with the other atom (see Fig. 4).

If the methyl group adds on to a $\pi$ system, the hydrogen group $H_3$ can be regarded as a speudoatom X, contributing one electron to the total pseudo-$\pi$ and the hyperconjugated system. Thus if $\psi_i$ denotes a $\pi$ orbital at the atom $i$, the molecular wave function for the energy level $k$ is written

$$\Phi_k = \sum_i C_{ik}\psi_i. \qquad (5.4)$$

where in the case of hyperconjugation some of the $\psi_i$ will be $\pi$ orbitals of the methyl carbon atom with the pseudoatom X.

The condition for normalisation of the wave function $\Phi_k$ allowing for overlap of the atomic orbitals $S_{ij} = \langle \psi_i | \psi_j \rangle$ is represented by

$$1 = \langle \Phi_k | \Phi_k \rangle = \sum_{ij} C_{ik}C_{jk} \langle \psi_i | \psi_j \rangle = \sum_{ij} C_{ik}C_{jk}S_{ij} = \sum_i C_{ik}Y_{ik}, \qquad (5.5)$$

where $Y_{ik} = \sum_j C_{jk}S_{ij}$.

If $\Phi_0$ is the wave function of the odd electron, its density at atom $k$ is given by the expression[68,69]

$$q_k = C_{k0}Y_{k0}. \qquad (5.6)$$

In this case this definition of odd-electron density is the same as McConnell's definition of spin density[12]. Here

$$\rho_k = \langle \Phi_0 | \Delta_k | \Phi_0 \rangle = \sum_{ij} C_{i0}C_{j0} \langle \psi_i | \Delta_k | \psi_j \rangle = C_{k0}Y_{k0}, \qquad (5.7)$$

where the operator $\Delta_k$ satisfies the equation

$$\Delta_k \psi_j = \delta_{jk}\psi_j, \qquad (5.8)$$

$\delta_{jk}$ being non-zero only if the electron $k$ is in orbital $j$. To this approximation the spin density should always be positive, which, as has been remarked several times, is not always the case.

Chesnut calculated the isotropic hyperfine coupling and the distribution of spin density for ethyl radicals using different values of the parameter $p$, which is taken as the ratio of two resonance integrals

$$p = \gamma_{ij}/\gamma_0, \text{ where } \gamma_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle \qquad (5.9)$$

and

$$p = \frac{\gamma_{ij}}{\gamma_0} = \frac{S_{ij}}{S_0}.$$

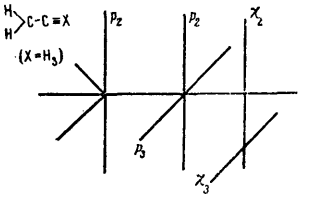



Fig. 4. Hyperconjugation in the ethyl radical.

Here $S_{ij}$ is the overlap of the atomic orbitals $i$ and $j$, while $S_0$ and $\gamma_0$ relate to values of these quantities for unsubstituted benzene [67]. The results of Chesnut's calculations are given in Table 3.

Table 3 shows that the hyperfine coupling constant does not decrease a great deal if more than one methyl group is involved in the hyperconjugation. This explains the dependence of the width of aliphatic radical spectra on the number of protons producing hyperfine splitting. The width of the spectrum can then be expected to increase with the number of groups involved in hyperconjugation at the carbon atom having the odd electron. The density $\rho_C$ at the central carbon atom varies little for a given value of $p$, and the hyperfine splitting is, to a good approximation, proportional to this spin density.

A series of radicals was studied experimentally by Symons [70], the spin densities being calculated by means of the McConnell equation, although Symons himself points out that the application of this equation is not entirely justified with aliphatic radicals when $\rho$ is large and both $\alpha$ and $\beta$ hydrogen atoms couple with the odd electron. Spin densities were estimated in this paper for the radicals $\cdot CH_3$, $\cdot C(CH_3)_3$, $\cdot CH_2CH_3$, and $\cdot CH(CH_3)_2$, and a series of radicals derived from alcohols: $\cdot CH_2OH$, $\cdot CH_2C(CH_3)_2OH$, $\cdot CH(CH_3).C(CH_3)_2OH$, $\cdot CH(CH_3)CH(CH_3)OH$, etc.

In a study of irradiated malonic acid [the $\cdot CH(COOH)_2$ radical] McConnell *et al.* [48] estimated the hyperfine splitting from the isotropic and anisotropic coupling and also estimated the spin density. They showed that $Q$ in the equation $a_H = Q\rho_C$ should be negative, as had previously been predicted theoretically, since it is only then that agreement is obtained between theoretical values of the hyperfine splitting and the experimental data.

This work was extended to a study of succinic acid [71] [the $.CH(COOH)CH_2COOH$ radical]. Here, as in Chesnut's work, consideration was given to the hyperfine coupling of the odd $\pi$ electron with a "$\pi$ proton", *i.e.* with a proton situated near the aliphatic carbon atom in a plane above or below the plane in which the $\pi$-electron spin density is distributed. In this work, however, anisotropic splitting of the "$\pi$ protons" was determined experimentally for the case in which there was no free rotation of these protons.

It is postulated that, similarly to the equation $a_N = Q\rho_N$ for $\sigma$ protons, the isotropic hyperfine coupling at the N nucleus with the "$\pi$ proton" is directly proportional to the spin density at the adjacent unsaturated carbon atom:

$$b_N = R(0)\rho_N. \tag{5.10}$$

The coefficient of proportionality depends on $\theta$, the angle of rotation of the alkyl group attached to the unsaturated carbon atom. The angle $\theta$ is defined so that $\theta = 0$ corresponds to the "eclipsed" configuration of the C–H bond relative to the axis of symmetry of the $\pi$ orbital of the odd electron, whereas $\theta = \frac{1}{2}\pi$ corresponds to the proton situated in the nodal plane of the odd-electron orbital. Thus when $\theta = \frac{1}{2}\pi$ the proton of the alkyl group is a "$\sigma$ proton". It is shown in the paper that the hyperfine splitting of the "$\pi$ proton" is almost isotropic, and therefore the mean value of $R(\theta) - < R >$ can be estimated. In the case of the radical $\cdot C(CH_3)_2OH$ the splitting amounts to 56 Mc/s, [72] which is probably the best value of $< R >$ at the present time. The angular variation of $R(\theta)$ can be approximately represented by the equation.

$$R(\theta) = A + B\cos^2\theta. \tag{5.11}$$

Theoretical calculations of hyperfine coupling of the protons of methyl groups [73] indicate that, when $\theta = \frac{1}{2}\pi$, $R \simeq 0$, and hence that $A = 0$. The experimental value of $B$ is then as follows

$$< R(\theta) > = {}^1/_2 B = 56 \text{ Mc/s},$$
$$B = 112 \text{ Mc/s}. \tag{5.12}$$

Isotropic splitting of the order of 112 $\cos^2 30^\circ$ = 84 Mc/s can be expected in this case for the "$\pi$ protons" in succinic acid, provided that the two protons are oriented exactly as in the non-irradiated molecule of the acid.

TABLE 3.

| Radical | Coupling constant of methyl protons | Spin densities | |
|---|---|---|---|
| | | $\rho_C$ | $\rho_X$ |
| $p = 0.7$ | | | |
| Ethyl | 16.9 | 0.9160 | 0.0815 |
| Isopropyl | 15.5 | 0.8433 | 0.0743 |
| t-Butyl | 16.2 | 0.7825 | 0.0684 |
| $p = 0.93$ | | | |
| Ethyl | 27.8 | 0.8577 | 0.1307 |
| Isopropyl | 24.2 | 0.7568 | 0.1137 |
| t-Butyl | 21.5 | 0.6807 | 0.1008 |

## 6. APPLICATION OF THE ALTERNANT ORBITAL METHOD

Papers have recently appeared in which the distribution of spin density is calculated by Löwdin's so-called alternant orbital method (AOM) [74–76]. The wave function with which the matrix elements of the spin density operator are calculated is obtained by applying the double state projection operator to the determinant

$$T_0 = |(a\Phi_1 + b\Phi_1')(a\Phi_2 + b\Phi_2')\ldots(a\Phi_n + b\Phi_n') \times$$
$$\times (a\bar{\Phi}_1 - b\bar{\Phi}_1')(a\bar{\Phi}_2 - b\bar{\Phi}_2')\ldots(a\bar{\Phi}_n - b\bar{\Phi}_n')|; \tag{6.1}$$
$$a = \cos\theta,\ b = \sin\theta,\ a^2 + b^2 = 1.$$

Here $\Phi$ is the wave function with spin $\alpha$, $\bar{\Phi}$ the wave function with spin $\beta$, $\theta$ a parameter which combines the excited configurations and the lowest molecular configurations, the $\Phi$ representing bonding orbitals, and $\Phi'$ antibonding orbitals.

According to Löwdin, the projection operator for $N$ particles having a spin of $\frac{1}{2}$ is

$${}^{2l+1}O = \prod_k^{k\neq l} (s^2 - k(k+1))/l(l+1) - k(k+1)). \tag{6.2}$$

The spin operator $s^2$ has the eigenvalues $l(l+1)$ where $l = \frac{1}{2}N$, $\frac{1}{2}N - 1$, ..., 0 or $\frac{1}{2}$ depending on whether $N$ is even or odd, and the product is to be taken over all $k \neq l$ from 0 or $\frac{1}{2}$ to $\frac{1}{2}N$.

Application of ${}^{2l+1}O$ to $T_0$ gives

$${}^{2l+1}OT_0 = \sum_{k=0}^{n} C_k' T_k, \tag{6.3}$$

and for the cases of lowest and highest multiplicity ($l = 0$ and $n$):

$${}^1OT_0 = C_0^{(0)} \sum_{k=0}^{n} (-1)^k \binom{n}{k}^{-1} T_k, \tag{6.4}$$

$${}^{n+1}OT_0 = C_0^{(n)} \sum_{k=0}^{n} T_k, \tag{6.5}$$

where $T_k = n(2k+1) - 2k^2$ is the sum of the determinants obtained by $k$ changes in the spin functions in $T_0$ between the two original groups of orbitals $\Phi_i$ and $\Phi_i'$. The value of $C_0$ is $\frac{2}{3}$ for three electrons, and $\frac{1}{2}$ for five electrons.

Application of the doublet operator yields

$$
\begin{aligned}
{}^2OT_0 = C_0 \sum_{k=0}^{n} (-1)^n \binom{n+1}{k} T_k = a^{2n} |\Phi_1\Phi_2 \ldots \Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i \ldots \overline{\Phi}_n| + \\
+ \left(\frac{2}{3}\right)^{1/2} a^{2n-1}b \sum_{i=1}^{n} \frac{1}{(6)^{1/2}} \{|\Phi_1\Phi_2 \ldots \Phi_i' \ldots \Phi_n\Phi_0\overline{\Phi}_1 \ldots \overline{\Phi}_n| - \\
- |\Phi_1\Phi_2 \ldots \Phi_i \ldots \Phi_n\overline{\Phi}_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i' \ldots \overline{\Phi}_n| + \\
+ 2|\Phi_1\Phi_2 \ldots \Phi_i \ldots \Phi_n\overline{\Phi}_0\overline{\Phi}_1 \ldots \overline{\Phi}_i' \ldots \overline{\Phi}_i' \ldots \ldots \overline{\Phi}_n|\} - \\
- \frac{(12)^{1/2}}{3} a^{2n-2}b^2 \sum_{i>j} \frac{1}{(12)^{1/2}} \{2|\Phi_1\Phi_2 \ldots \Phi_i\Phi_i'\Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_j' \ldots \overline{\Phi}_j \ldots \overline{\Phi}_n| + \\
+ 2|\Phi_1\Phi_2 \ldots \Phi_j' \ldots \Phi_i\Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i \ldots \overline{\Phi}_j' \ldots \overline{\Phi}_n| - \\
- |\Phi_1\Phi_2 \ldots \Phi_i' \ldots \Phi_j' \ldots \Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i\overline{\Phi}_j \ldots \overline{\Phi}_n| + \\
+ |\Phi_1\Phi_2 \ldots \Phi_i' \ldots \Phi_j \ldots \Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i\overline{\Phi}_j' \ldots \overline{\Phi}_n| + \\
+ |\Phi_1\Phi_2 \ldots \ldots \Phi_i \ldots \ldots \Phi_j' \ldots \Phi_n\Phi_0\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i\overline{\Phi}_j \ldots \overline{\Phi}_n| - \\
- |\Phi_1\Phi_2 \ldots \Phi_i \ldots \Phi_j \ldots \Phi_i' \ldots \Phi_j' \ldots \overline{\Phi}_n|\} - \\
- a^{2n-2}b^2 \sum_{i=1}^{n} \{|\Phi_1\Phi_2 \ldots \ldots \Phi_i' \ldots \Phi_j \ldots \Phi_n\overline{\Phi}_1\overline{\Phi}_2 \ldots \overline{\Phi}_i'\overline{\Phi}_j \ldots \overline{\Phi}_n|\}.
\end{aligned}
\tag{6.6}
$$

For normalisation, this function must be divided by $N^{\frac{1}{2}}$, where

$$N = a^{4n} + (2n/3)\, a^{4n-2}b^2 + a^{4n-4}b^4 (2n^2+n)/3. \tag{6.7}$$

On calculating by means of the expectation value of the spin density operator

$$1/m_s \sum_{\mu} \delta(r - r_\mu) S_{\mu z}$$

for the molecular-orbital spin density, we obtain

$$
\begin{aligned}
\rho(r) = N^{-1} \left\{ a^{4n}\delta_{00} + \frac{4}{3} a^{4n-1}b \sum_{i=1}^{n} \delta_{ii'} + \frac{1}{9} a^{4n-2}b^2 \times \right. \\
\left. \times \sum_{i=1}^{n} [4\delta_{ii'} - 2\delta_{00} + 4\delta_{ii}] + \left(\frac{8}{9}n + \frac{4}{9}\right) a^{4n-3}b^3 \times \sum_{i=1}^{n} \delta_{ii'} + [(2n^2+n)/3]\, a^{4n-4}b^4\delta_{00} \right\},
\end{aligned}
\tag{6.8}
$$

where

$$\delta_{00} = \Phi_0^2(r), \quad \delta_{ik} = \Phi_i(r)\,\Phi_k(r), \quad \delta_{ii'} = \Phi_i(r)\,\Phi_i'(r).$$

If we pass to atomic-orbital spin density and represent by $\rho_A$ the spin density at the starred atoms, and by $\rho_B$ the density at the non-starred atoms, we obtain the following relations:

$$\rho_A = (N')^{-1} \left\{ C_{0A}^2 Y + \frac{2}{3}\tan\theta + \frac{4}{9}\tan^2\theta + [(4n+2)/9]\tan^3\theta \right\} \chi_A^2(r), \tag{6.9}$$

$$\rho_B = (N')^{-1} \left\{ -\frac{2}{3}\tan\theta + \frac{4}{9}\tan^2\theta - [(4n+2)/9]\tan^3\theta \right\} \chi_B^2(r), \tag{6.10}$$

$$N' = 1 + (2n/3)\tan^2\theta + [(2n^2+n)/3]\tan^4\theta, \tag{6.11}$$

$$Y = 1 - \frac{2}{3}\tan\theta - [(2n+4)/9]\tan^2\theta - [(4n+2)/9]\tan^3\theta + [(2n^2+n)/3]\tan^4\theta. \tag{6.12}$$

It can be shown that $\tan\theta$ is always positive, so that the sign of $\rho_B$ will depend on that of the right-hand expression. In Eqns. (6.9)–(6.12), $\chi_A(r)$ represents an atomic orbital centred on a starred atom A, while $\chi_B(r)$ represents an atomic orbital on a non-starred atom B.

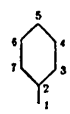
These formulae were used to calculate spin densities in alternant hydrocarbon radicals containing an odd number of carbon atoms: triphenylmethyl, perinaphthenyl[75], and allyl[76].

In the triphenylmethyl calculation terms of the order of $b^2$ were neglected, so that

$$\rho_A = \left(1 - \frac{2}{3}\tan\theta\right) C_{0A}^2 + \frac{2}{3}\tan\theta,$$

$$\rho_B = -\frac{2}{3}\tan\theta.$$

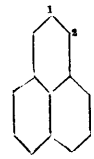
The parameter $\theta$ was calculated from the experimental value of the spin density at a non-starred atom, its value was substituted in $\rho_A$, and the result was compared with experiment. Reitz showed that for triphenylmethyl[77] $|\rho_3| = |\rho_5| = 2|\rho_4|$. It follows from Adam and Weissman's work[57] that the sum of the absolute spin densities at all the carbon atoms linked to a proton is $\rho = 1.57$. On comparing the results, we obtain




$$3\{2|\rho_3| + 2|\rho_4| + |\rho_5|\} = 24|\rho_4| = 1.57, \quad |\rho_4| = 0.065,$$
$$\rho_4 = -0.065.$$

Then $\rho_3 = \rho_5 = 0.137$.

For the perinaphthenyl radical[10], the measured spin density is $|\rho_1| = 0.098$. According to the alternant orbital method, $\rho_1 = -0.098$, whence $\rho_2 = 0.2477$ (the experimental value is $\rho_2 = 0.327$).




With the allyl radical the spin densities obtained by the alternant orbital method showed good agreement with those calculated by the configurational interaction method[32]:

| AOM | Configuration interaction |
|---|---|
| $\rho_1 = 0.6388$ | $\rho_1 = 0.6363$ |
| $\rho_2 = -0.2645$ | $\rho_2 = -0.2334$ |
| $\rho_3 = 0.6588$ | $\rho_3 = 0.6363$ |

## 7. SPIN DENSITY AND NUCLEAR MAGNETIC RESONANCE

As McConnell[12] has shown, the magnitude and sign of the spin density can be judged from the chemical shift developed in the proton magnetic resonance of paramagnetic substances. The chemical shift $\Delta H$ at the proton and the spin density $\rho_C$ at the carbon atom adjacent to the proton are related as follows:

$$\Delta H = Q\rho_C(\gamma_e/\gamma_H)\, g\beta S(S+1)/6kT, \tag{7.1}$$

where $Q$ is the proportionality constant in the McConnell equation, $\gamma_e$ and $\gamma_H$ represent the gyromagnetic ratio for the electron and the proton respectively, $g$ is the spectroscopic splitting factor, $\beta$ the Bohr magneton, $k$ the Boltzmann constant, $T$ the absolute temperature, and $S$ the spin of the odd electron. A paper by Lefebvre[78] gives a theoretical derivation of this equation and discusses the form of the proton resonance line in polycrystalline radicals.

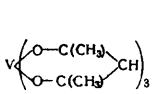
Eqn. (7.1) was first used to estimate spin densities in the organometallic compounds vanadocene, chromocene, and nickelocene [79,80]. In contrast to nickelocene, in which the spin density at the carbon atoms in the ligands is positive, that in the ligands of vanadocene and chromocene was found to be negative with values of $\rho_C$ = -0.06 and -0.12 respectively. The sign of the spin density is determined by the direction of the chemical shift at the proton. If the spin of the proton is polarised in the direction of the external magnetic field, the shift takes place towards lower fields. If the proton spin is in the direction opposite to the applied magnetic field, the proton shift occurs at higher values of the magnetic field.

Nuclear magnetic resonance made it possible to determine spin densities in diphenylpicrylhydrazyl [17,81]. The resonance line of this radical consisted of two partly resolved components of equal intensity but different widths, one being shifted to increasing field by 2.95 oersteds, while the other is shifted in the opposite direction by 1.75 oersteds. As already remarked, the spin polarisation of the proton is opposite to that of the adjacent carbon (or nitrogen) atom [48]. Therefore the sign of the proton shift should be the same as that of the spin density $\rho_C$, as is reflected in Eqn. (7.1) ($Q$ = -22.5). If one line (up the field) is assigned four *ortho*- and two *para*-protons, while the narrower line is given six *meta*-protons, the shift agrees with calculations on diphenylpicrylhydrazyl by the valence bond method, according to which the spin densities in the *ortho*- and *para*-carbon positions are positive, while those in the *meta*-position are negative. These results confirm not only the existence of negative and positive spin densities, but also the sign of the equation $a = -22.5\rho_C$.

Anderson *et al.* [82] studied the shifts in nuclear magnetic resonance of the negative pyrene ion in its potassium compound, and estimated the isotropic hyperfine coupling constants. The values obtained were very close to those obtained from experiments on electron paramagnetic resonance. Some divergence in the values of the constants was partly due, in the opinion of the authors, to a change in the odd-electron density distribution in the ion under the influence of the crystal lattice, accompanied by corresponding changes in the $\pi-\sigma$ exchange, giving isotropic hyperfine splitting. The difference may be due also to the anisotropy observed in the proton resonance lines.

An interesting confirmation of the fact that the spin density at protons of the methyl group in the C–$CH_3$ bond is opposite in sign to the spin density at the proton in the C–H bond (in electron paramagnetic resonance this is reflected in the sign of $Q$ = 25 oersteds for the former, and of $Q$ = = -22.5 oersteds for the latter case) is given in a paper by Forman *et al.* [83], who investigated the proton shifts for vanadium acetylacetonate. Compared with the diamagnetic cobalt acetylacetonate, the vanadium compound exhibits a shift towards lower fields.

When the hydrogen in the third position in



is replaced by a methyl group, the shift is changed markedly, owing to the change in the distribution of spin density at this position. Since the shifts are opposite, it is clear that the spin densities at the protons in the C–$CH_3$ and C–H groups have different signs.

Similar results were obtained for the distribution of spin density in the ligands of nickel chelates [84]. Changes in the distributions of spin density in such compounds produced by the introduction of heteroatoms (S and O) into the system of conjugated bonds, and by –NH– and –N : N– groups have been determined by nuclear magnetic resonance [85].

Thus the distribution of spin density may also be successfully studied in inorganic molecules. The use of nuclear magnetic resonance for this purpose has started comparatively recently, but from the work which has been done up to the present time it can already be concluded that further investigations by this method on paramagnetic compounds, in particular on paramagnetic aromatic complexes of metals, will undoubtedly be of great value in elucidating their electronic structure.


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