The author would like to express his deep appreciation to P. Nikolai and W. L. McDavid of these laboratories for invaluable assistance in numerical analysis and programming phases of this work, and would also like to acknowledge that the computations were performed on the IBM 7090 computer of the Aeronautical Systems Division, Wright–Patterson Air Force Base, Ohio.

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# Spin Resonance and Hyperfine Interaction

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## INTRODUCTION

THIS paper is restricted to electron spin resonance phenomena in free radicals. We shall choose a few topics in which significant advances have been made recently, especially topics reflecting more directly on some aspects of electron correlation. We shall, therefore, largely be concerned with discussing the electron spin resonance (ESR) spectra of organic free radicals. These species exhibit electron spin resonance because they have an unpaired $\pi$ electron.

The spin Hamiltonian $\mathcal{H}$ for a system of $\pi$ electrons such as one has in a $\pi$-electron radical can be written as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 , \tag{1}$$

where

$$\mathcal{H}_1 = \mathcal{H}_0 + \beta \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} \tag{2}$$

and

$$\mathcal{H}_2 = g_e\beta_e g_N\beta_N \sum_{\lambda,\mu}\left[-\frac{\mathbf{S}_\lambda\cdot\mathbf{I}_\lambda}{r^3_{\lambda\mu}} + 3\,\frac{(\mathbf{r}_{\lambda\mu}\cdot\mathbf{S}_\lambda)(\mathbf{r}_{\lambda\mu}\cdot\mathbf{I}_\mu)}{r^5_{\lambda\mu}}\right] + \frac{8\pi}{3}\,g_e\beta_e g_N\beta_N \sum_{\lambda\mu}(\mathbf{S}_\lambda\cdot\mathbf{I}_\mu)\,\delta(\mathbf{r}_{\lambda\mu}) . \tag{3}$$

For radicals in solution (or in the gas phase) the term between [ ] in Eq. (3) averages out to zero,[1] so for these cases the second term, the Fermi contact interaction which is isotropic, is important and gives rise to the hyperfine splitting observed for free radicals in solution. Weissman[1] neglected spin-orbital interaction effects which can also lead to isotropic hyperfine splittings for radicals in solutions[2]; but the effects are about 100 times too small to account for any of the observed splittings in aromatic free radicals. Considering, therefore, only the hyperfine interaction between the $z$ components of the electron and nuclear spins (valid in the Paschen–Back region), the Fermi contact Hamiltonian which gives the nonvanishing isotropic hyperfine splitting for free radicals in solution is

$$\mathcal{H}_N = \frac{8\pi g|\beta|}{3}\left(\frac{\mu_N}{I}\right)\sum_k S_{kz}I_{Nz}\,\delta(\mathbf{r}_{kN}) . \tag{4}$$

In Eq. (4) $|\beta|$ is the absolute magnitude of the Bohr magneton, $\delta(\mathbf{r}_{kN})$ is the Dirac delta function of the distance $\mathbf{r}_{kN}$ between electron $k$ and nucleus $N$, $\mu_N$ is the magnetic moment of proton $N$, and $I_{Nz}$ is the $z$ component of the spin of proton $N$, in units of $\hbar$. This equation can be expressed more simply in terms of the "coupling constant" for the proton $N, a_N$ as

$$\mathcal{H}_N = h a_N S_z I_{Nz} . \tag{5}$$

## SPIN DENSITIES IN $\pi$-ELECTRON RADICALS

Equation (5) is frequently written in the form introduced by McConnell[3]

$$a_N = Q\rho_N . \tag{6}$$

Here $Q$ is negative and has been given various values such as $-22.5$ G for the benzene negative ion,[4] $-25.67$ G for the cyclooctatetraene radical anion,[5] and values of about $-30$ G,[6] which are necessary to fit the observed electron spin resonance spectra of polynuclear hydrocarbon radical ions, if it is assumed that the odd electron densities $\rho_N$'s are given by the

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[3] H. M. McConnell, J. Chem. Phys. **24**, 632, 764 (1956).

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simple Hückel LCAO molecular orbital theory. Equation (6) would predict that the total width of the esr spectrum of a free radical would be $\sum \rho_N = 2S$ where $S$ is the total spin. If only positive values of $\rho_N$ are allowed, as in the simple Hückel LCAO theory, then the total width of the ESR spectra would be $Q$ gauss since $\rho_N$ (Hückel) $= 1$. Spectra are observed, however, to extend over a range greater than 25–28 G, and it must, therefore, be concluded that $\rho_N$ may be either positive or negative. Brovetto and Ferroni[7] were the first to propose, on theoretical grounds, that the proton hyperfine splittings in the triphenyl methyl radical can be positive and negative as a result of their valence-bond calculations carried out for the assumed planar structure of this radical. Negative spin densities have been shown to be necessary in the interpretation of the electron-spin-resonance spectra of aromatic radicals by McConnell and Chesnut[8] who, as mentioned above, have given a detailed theoretical treatment of the isotropic hyperfine interactions in $\pi$-electron radicals[2] and have shown that in Eq. (6) the spin density can assume positive or negative values. Equation (6) must then be written as $a_N = Q|\rho_N|$.

McConnell has shown[9] that Eq. (6) is the approximate form of a more elaborate Eq. (7):

$$a_N = \mathrm{Tr}(Q^N \rho) \,, \tag{7}$$

where $Q^N = Q^N_{N'N''}$ is a hyperfine-interaction–exchange-interaction matrix and $\rho(=\rho^{NN'})$ is a spin-density matrix. It is readily shown that the largest term in the matrix $Q^N_{N'N''}$ is the diagonal element $Q^N_{NN}$ and it can, to a first approximation, be assumed to be the same for all carbon atoms in a $\pi$-electron system. Thus, the form of Eq. (6) which results is $a_N = Q\rho_{NN}$, where $Q = Q^N_{NN}$, and $\rho_{NN}$ represents the diagonal elements of the spin-density matrix $\rho_{NN'}$.

If the eigenfunction $\Psi$ for the $\pi$-electron system is expressed in terms of orthonormal molecular orbital functions $\Phi_i$, then the normalized spin-density function $\rho(x,y,z)$ can be developed in terms of the molecular orbital density matrix $\bar{\rho}_{ij}$:

$$\rho(x,y,z) = \sum\nolimits_{ij} \bar{\rho}_{ij} \Phi_j^* \Phi_i \,. \tag{8}$$

When $\Psi$ is expressed in terms of a set of normalized atomic orbitals $\phi_\lambda$, which are not necessarily orthonormal, the atomic orbital density matrix $\rho_{\lambda\mu} = \rho$ can be defined as

$$\rho(x,y,z) = \sum\nolimits_{\lambda\mu} \rho_{\lambda\mu} \phi_\mu^* \phi_\lambda \,. \tag{9}$$

The matrices $\bar{\rho}$ and $\rho$ can be related to one another when the molecular orbitals $\Phi_i$ are expressed as linear combinations of atomic orbitals,

$$\Phi_i = \sum\nolimits_\lambda a_{\lambda i} \phi_\lambda \,; \tag{10}$$

then

$$\rho_{\lambda\mu} = \sum\nolimits_{ij} \bar{\rho}_{ij} a_{\mu j}^* a_{\lambda i} \,. \tag{11}$$

If electron correlation is neglected as in simple molecular orbital theory where the eigenfunction of the molecule (radical) is written as a single configuration, all the nondiagonal elements $\bar{\rho}_{ij}$ are zero, and the diagonal elements are positive. Thus, when no electron correlation effects are included in the eigenfunction, the spin density $\rho$ is positive everywhere. Under these conditions the diagonal elements of $\rho_{\lambda\mu}$ are also positive but the nondiagonal elements may be negative.

When electron correlation is included, as it is particularly in the case of free radicals, the matrix $\bar{\rho}_{ij}$ is nondiagonal because of the configuration interaction. Both diagonal and nondiagonal elements can now be negative. With electron correlation included, some of the diagonal elements of $\rho_{\lambda\mu}$ may be negative which implies that the spin density $\rho(x,y,z)$ can be negative at all points in the vicinity of one atom. By the application of this theory to the allyl radical $(\cdot CH_2 \cdot CH \cdot CH_2)$, McConnell,[9] using the eigenfunctions calculated by Chalvet and Daudel,[10] showed that there was a negative spin density on the central carbon atom $C_2$ of $\rho_{22} = -0.1055$.

The simple Hückel LCAO molecular orbital theory provides a useful first approximation interpretation of the ESR spectra of many radicals, though it cannot yield negative spin densities. In those cases where negative spin densities do not arise, or when they are of very small magnitude, then the Hückel simple LCAO theory is still useful. It has been used with some success in the interpretation of the ESR spectra of many ion radicals such as those of benzene,[11] naphthalene,[12] anthracene,[12] diphenyl,[12] etc.,[13–17] and

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in heterocyclic anions,[18–22] many semiquinone ions,[21–27] the cation of phenylene diamine,[28] and many other cases.

Although there was good agreement between the simple Hückel LCAO molecular orbital theory and the experimental results for many ions of even alternate hydrocarbons, there were some serious discrepancies. It must also be recalled that the simple Hückel theory did not lead to a correct calculation of the over-all width of the ESR spectra of these radicals.

Two cases where it became most apparent that negative spin densities were necessary to explain the observed spectra may now be discussed. The first case is that discussed by Hoijtink, Townsend, and Weissman,[29] who drew attention to the serious discrepancy existing in the case of the anion of pyrene. The simple Hückel theory predicts that the singly occupied orbital in the anion is antisymmetric in the plane passing through positions 2, 12, 15, and 7 (see Fig. 1), and yields a splitting into 25 lines by the two sets of equivalent protons at positions 1, 3, 6, and 8 and 4, 5, 9, and 10. High resolution studies yielded a well-resolved 75-line spectrum which is required if there is also some spin density on carbon atoms 2 and 7. The spectrum is well represented by the assignment of the coupling constants of 4.75 and 2.08 G to the protons of types 1 and 4, respectively, and a coupling constant of $-1.09$ G for the protons of type 2.

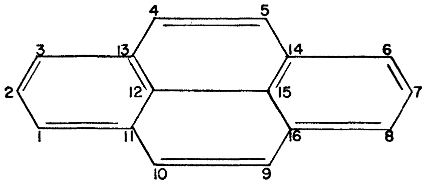

FIG. 1. The pyrene molecule.

A simple configuration interaction treatment based on earlier studies by Hoijtink[30] leads to results in good agreement with the experimentally observed spectrum. The principal configuration of the ground state of the pyrene anion with $2n$ carbon atoms is represented by the antisymmetrized product

$$\Psi_N = |\psi_1\bar{\psi}_1\cdots\psi_j\bar{\psi}_j\cdots\psi_{n+1}| \,. \tag{12}$$

In this equation each $\psi$ is taken as a linear combination of atomic orbitals $\phi$, i.e.,

$$\psi_j(v) = \textstyle\sum_s c_{sj}\phi_s(v) \,. \tag{13}$$

Inclusion of doubly excited configurations of the type

$$\Psi_v = 6^{-\frac{1}{2}}\{2|\psi_j\bar{\psi}_{n+1}\psi_k| - |\psi_j\bar{\psi}_k\psi_{n+1}| + |\psi_k\bar{\psi}_j\psi_{n+1}|\} \times j \leqslant n; \quad k \geqslant n+2 \,, \tag{14}$$

which interacts with $\Psi_N$, leads to nonvanishing spin densities at those carbon atoms $t$ where the spin density vanishes when $\Psi_N$ alone is used (i.e., at carbon atoms 2 and 7). $\rho_t$ is given by the following equation on the application of first-order perturbation theory:

$$\rho_t = 2\sum_j\sum_k \frac{\langle j,n+1|k,n+1\rangle}{E_v - E_N} c_{tj}c_{tk} \,. \tag{15}$$

As self-consistent field orbitals were not available, Hoijtink, Townsend, and Weissman used Hückel orbitals. Equation (15) shows that if $\rho_t$ is not to be zero, the matrix element and the coefficients $c_{tj}c_{tk}$ must not vanish. The pairs of Hückel orbitals for pyrene with $j = 7$, $k = 13$ and $j = 4$, $k = 10$ contribute strongly to the spin densities at positions 2 and 7. Using appropriate one-electron excitation energies the spin densities at positions 2 and 7 are found to be $\rho_2 = \rho_7 = -0.039$. These results, with $Q = 27$ G, on substitution into Eq. (6) give the coupling constant at positions 2 and 7 as $-1.05$ G which is in good agreement with the experimentally required value.

A theoretical interpretation of the esr spectrum of the dimesityl methyl radical (Fig. 2) in toluene solution was given by McLachlan,[31] who used a modified valence-bond treatment.

If $K$ is the exchange integral between the carbon atoms in the rings and the control carbon atom C(1), the use of perturbation theory with the perturbation $H' = -\frac{1}{2}K(1+\sigma_1\sigma_2)$ yields the following expression

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[31] A. D. McLachlan, J. Chem. Phys. **32**, 1488 (1960).

for the spin density $\rho_r$ at carbon atom $r$:

$$\rho_r = \sum_{n=0} \frac{\langle 0|K\sigma_{z2}|n\rangle\langle n|\sigma_{zr}|0\rangle}{E_n - E_0}. \tag{16}$$

$\psi_0$ is taken to be the exact valence-bond ground singlet state of benzene, and $\psi_n$ to be the other nine excited triplet states. The exchange integral $K = J\cos^2\alpha$, where $\alpha$ is the angle of twist of the rings and is 60°–70°, and $J$ is the exchange integral between ring carbon atoms.

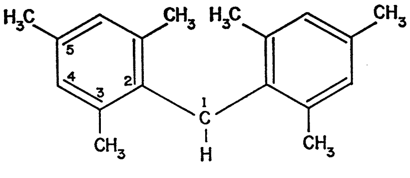

FIG. 2. The dimesitylmethyl radical.

This theoretical treatment yields a negative spin density at carbon atom 2 of $-0.263$ if $\alpha = 0°$, and $-0.069$ if $\alpha = 60°–70°$. The agreement between the "observed" or experimental spin densities[32] and the calculated values is not wholly satisfactory; it does not provide evidence for the existence of negative spin densities nor support a nonplanar configuration for the dimesityl methyl radical.

In addition, McLachlan[31] has developed a self-consistent-field molecular orbital theory of electron spin distribution in $\pi$-electron radicals. This theory yields negative spin densities at certain positions in neutral alternate hydrocarbon radicals and also in the anions and cations of alternate hydrocarbons. The calculated over-all spectral widths are in good agreement with the experimentally observed values. McLachlan writes the wave function for radicals as

$$\chi_0 = ||\psi_1^2\psi_2^2\cdots\psi_n^2\psi_0^\alpha||, \tag{17}$$

in which $2n$ electrons occupy the orbitals $\psi_1\cdots\psi_n$ in pairs and the odd electron with spin $\alpha$ is in the $\psi_0$ orbital. Because this wave function (17) is not self-consistent in the full sense, a more elaborate form due to Pople and Nesbet[33] is used. These authors proposed the self-consistent wave function

$$\Phi = ||\psi_1^\alpha\psi_1'^\beta\cdots\psi_n^\alpha\psi_n'^\beta\psi_n^\alpha||, \tag{18}$$

in which electrons of $\alpha$ and $\beta$ spin occupy independent sets of orbitals $\psi_0$, $\psi_1\cdots\psi_n$ and $\psi_1'\cdots\psi_n'$. For this type of wave function the spin density is given by Eq. (19):

$$\rho = |\psi_0|^2 + \sum_1^n \{|\psi_i|^2 - |\psi_i'|^2\}, \tag{19}$$

so that if $|\psi_i'|^2$ is greater than $|\psi_i|^2$ at a node of $\psi_0$, $\rho$ becomes negative. McLachlan[34] showed that using the LCAO semiempirical method of Pariser and Parr,[35] with the notation and approximations of Pople and Brickstock,[36] the following equation is obtained for the spin densities:

$$\rho_r = c_{0r}^2 - \tfrac{1}{2}\gamma \sum \pi_{rs}c_{0s}^2, \tag{20}$$

where $C_{0r}$ and $C_{0s}$ are the coefficients of the two sets of LCAO orbitals

$$\psi_0 = c_{0r}\phi_r, \psi_1 = c_{ir}\varphi_r, \psi_i' = c_{ir}'\phi_r. \tag{21}$$

If Hückel orbitals are used, the term $\frac{1}{2}\gamma$ in Eq. (21) is replaced by the empirical constant $\lambda$ which has a value $\approx 1.0–1.2\,\beta$. $\pi_{rs}$ is the mutual polarizability of the two atoms $r$ and $s$ and can be calculated from the expression

$$\pi_{rs} = -4\sum_i\sum_j \frac{c_{ri}c_{sj}c_{si}c_{rj}}{E_j - E_i}, \tag{22}$$

where $i,j$ are occupied and vacant orbitals. Applying this theory to a series of alternant hydrocarbon anions it was found to lead to the prediction of negative spin densities at certain positions in the radicals. Further it was possible using values of $\lambda = 1.0$ and $Q = -24.2$ G to obtain good agreement between the calculated and experimental values for the over-all widths of the ESR spectra of many ions. Table I gives the results and it is evident that the theory is fairly satisfactory.

TABLE I. Widths of ESR spectra of hydrocarbon anions.

| Anion | Obs. width (G) | Calc. width (G) |
|---|---|---|
| Benzene | 22.5 | 24.2 |
| Naphthalene | 26.9 | 26.0 |
| Diphenyl | 23.8 | 22.4 |
| Anthracene | 28.4 | 26.9 |
| Phenanthrene | 24.5[a] | 27.1 |
| Perylene | 28.3 | 28.1 |
| Pyrene | 31.2[a] | 29.5 |
| Acenaphthylene | 29.2[a] | 28.1 |
| Fluoranthene | 21.9[a] | 21.5 |

[a] Spectra incompletely resolved. Width is average of that between the ends of the derivative curve and that between the extreme peaks.

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## NUCLEAR MAGNETIC RESONANCE EVIDENCE FOR NEGATIVE ELECTRON-SPIN DENSITIES

Evidence from nuclear magnetic resonance studies points to the existence of negative electron-spin densities at certain atomic centers in paramagnetic molecules and free radicals. McConnell and Holm[37] observed that the proton resonance in polycrystalline nickelocene, and also for the same compound in toluene solution, was shifted $\sim 1.0 + 0.02$ G to higher fields relative to the normal resonance for protons in toluene. Later, Gutowsky and his colleagues [38,39] found that the proton magnetic resonance spectra of solid free radicals such as DPPH and trio-*p*-chlorophenylaminium perchlorate (TPPAP) at 77°K showed two different resonance lines, one shifted up-field and one down-field from the normal resonance frequency.

The origin of the shift in the proton magnetic resonance line can be understood from the simple theory due to McConnell and Chesnut.[2] In a system of protons characterized by a paramagnetic relaxation time $T_1$, or an exchange time $T_e$ such that $T_1^{-1}$ or $T_e^{-1} \gg a_N$ (the hyperfine splitting constant), then proton $N$ will see a single average hyperfine magnetic field corresponding to the effective spin Hamiltonian for proton $N$,

$$\mathcal{H} = -\mu_{Nz}\{H_0 - 2\pi a_N (I\hbar/\mu_N)\langle S_z\rangle\} \,, \tag{23}$$

where $\langle S_z\rangle$ is the time-average value of the $Z$ component of the electron spin. For paramagnetic molecules or radicals obeying the Curie law,

$$\langle S_z\rangle = -g|\beta|S(S+1)H_0/3kT \;; \tag{24}$$

hence,

$$\mathcal{H} = -\mu_{Nz}\left[1 + 2\pi a_N\left(\frac{I\hbar}{\mu_N}\right)\frac{g|\beta|S(S+1)}{3kT}\right]H_0 \,. \tag{25}$$

Since $\mu_N$ is positive for the proton, it is seen from Eq. (25) that when the proton resonance of $N$ is observed at a fixed frequency, the contact shift will be to lower applied fields when $a_N$ is *positive*, and to higher applied fields when $a_N$ is *negative*. The experimental results quoted above substantiate these theoretical requirements. Furthermore, a valence bond treatment yields positive densities at the *ortho* and *para* carbon atoms in the benzene rings and a negative spin density at the *meta* atoms. These results agreed with the assignment of the large up-field shift of the proton resonance to the *ortho* and *para* protons. Similar results have been obtained for proton resonance measurements on DPPH at 4.2°K by Anderson, Pake, and Tuttle,[40] and also by Hervé, Reimann, and Spence.[41] Proton resonance shifts have also been observed in the pyrene anion at 4.2°K by Anderson, Zandstra, and Tuttle,[42] who assign the positive proton coupling constant to the protons at positions 2 and 7 which, from Eq. (25), implies negative spin densities at the corresponding carbon atoms.

High-resolution proton magnetic resonance studies on paramagnetic molecules have also shown shifts in the positions of the resonance lines from which values for electron densities at different carbon atoms can be calculated. We have already mentioned the studies of McConnell and Holm on nickelocene in toluene solution at room temperature.[37] Qualitative studies[43] of the same sort have been made on vanadium *tris*-acetonylacetate. These studies indicate that the sign of the spin densities for directly attached hydrogen atoms is opposite to that for the hydrogen atoms of the methyl group.

Recently, high-resolution nuclear magnetic resonance studies on a large number of nickel (II) chelates have been reported by Eaton, Josey, Phillips, and Benson.[44–46] From the observed shifts, these workers have estimated electron densities at various positions in the compounds studied. They have attempted to interpret their findings in terms of calculations of the spin densities from valence-bond theory. Valence-bond theory was used for the nickel (II) aminotroponeimineates because these systems are nonalternant, and also because negative spin densities were predicted from the nuclear magnetic resonance studies.

There is evidence that spin density in these chelates is transferred from the nickel atom to the ligands as a result of metal–ligand $\pi$ bonding. Valence-bond cal-

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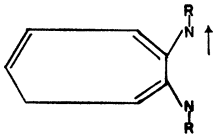
culations carried out for the ligand fragment



in which *R* is a nonconjugated substituent, i.e., $CH_3$ or $C_2H_5$, yield the values for the spin densities shown in Fig. 3.

The results quoted show that if the calculated spin densities are reduced by a factor of 10, there is good agreement between theory and experiment. The valence-bond method, thus, seems to be a useful approximation for estimating spin densities in these nonalternant systems. The scaling factor of 1/10 required to bring the calculated and experimental results into agreement represents the total spin density transferred from the metal atom to the $\pi$-electron system of each ligand.

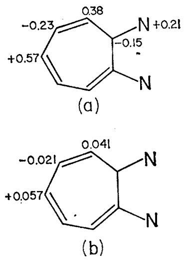


FIG. 3. (a) Theoretical spin densities; (b) experimental spin densities for nickel (II) aminotroponcimineate.

### LINEWIDTH VARIATIONS IN THE ELECTRON RESONANCE SPECTRA OF FREE RADICALS IN SOLUTION

Having outlined the experimental evidence showing the existence of negative spin densities in free radicals, as well as discussing the theoretical interpretation of the results, we must now turn to consider other phenomena which sometimes arise because of negative spin densities. The ESR spectra of many free radicals in solution consist of large numbers of lines which are often quite narrow ~ 20–100 mG. A subject of considerable current interest is the study of relaxation mechanisms in the narrow line systems. Frequently the spectra are asymmetrical as corresponding components on the high- and low-field sides of the spectra may have differing apparent intensities and linewidths. We now discuss theories of the origins of these asymmetries and their dependence on the form of the hyperfine interaction and *g*-value tensors. In several cases the observed linewidth variations of the various hyperfine components indicate that at least the isotropic coupling constants have opposite signs due to the existence of positive and negative spin densities in the radicals.

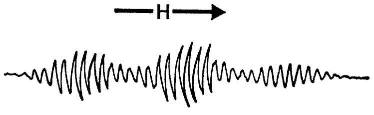


FIG. 4. The electron spin resonance spectrum of the diphenyl nitric oxide radical.

One fairly simple spectrum which exhibits asymmetry and variations of linewidth is that of diphenyl nitric oxide as reported by Deguchi.[47] Figure 4 shows a diagrammatic representation of this spectrum.

The lines in the central group are the sharpest compared with the outer groups. Each line on the low-field side is sharper than the corresponding one on the high-field side. Another particularly interesting example is the esr spectrum of the monopositive ion of pyracene in concentrated $H_2SO_4$. Pyracene (Fig. 5) is a novel hydrocarbon which has two sets of equivalent protons. The spectrum consists of nine groups of quintuplets and, as it is well resolved, the analysis is quite straightforward.[48] Within any one of the quintuplets, the component on the high field of the central line is smaller and wider than the corresponding mem-

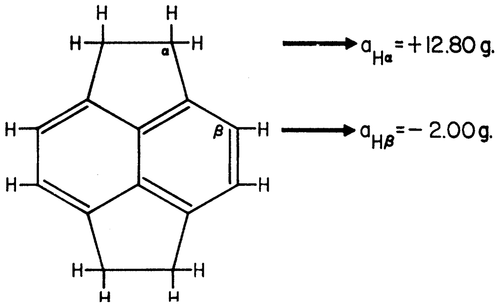


FIG. 5. The pyracene molecule.

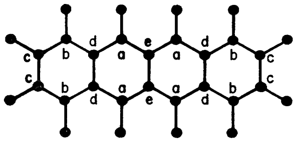


FIG. 6. The tetracene molecule.

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[47] Y. Deguchi, Bull. J. Chem. Soc. **35**, 260 (1962).

[48] E. de Boer and E. L. Mackor, Mol. Phys. **5**, 493 (1962).

ber on the low-field side. A somewhat similar variation in the intensities of the hyperfine components was found for the case of the ESR spectrum of the tetracene (see Fig. 6) positive ion in concentrated $H_2SO_4$.

In the tetracene positive ion there are obviously three classes of protons each with four protons in each class. Of the expected 125 lines 85 were found by Hyde and Brown[49]; the occurrence of accidental degeneracies being largely responsible for this discrepancy. An analysis of the spectrum which was observed at room temperature shows that lines 5 and 15 from the central line are narrower on the high-field side and correspondingly seem more intense than are lines 5 and 15 on the low-field side; the reverse was found to be true for line 3.

Similar variations in linewidths and hence intensities of certain hyperfine components have also been observed in the case of the negative ions of *m*-dinitrobenzene by Freed, Rieger, and Fraenkel[50] and independently by Fischer and McDowell.[51] In these cases the anion of *m*-dinitrobenzene was prepared by electrochemical reduction. Fraenkel *et al.* used *N*,*N*-dimethyl-formamide as a solvent and obtained their spectrum at −50°C. Fischer and McDowell used a 50–50% mixture of *N*,*N*-dimethyl-formamide and dimethoxyethane and obtained a completely resolved 60-line spectrum at room temperature. The spectrum obtained (see Fig. 7) can be analyzed completely and the analysis shows that the hyperfine components corresponding to $M_N = \pm 1$ are considerably broader and correspondingly appear to be less intense than those for which $M_N = 0, \pm 2$. Here $M_N$ is the total $z$ component of the nitrogen nuclear spin angular momentum.

Rather large anomalous alternating linewidths were observed in the ESR spectra of 1:4 dinitrotetramethylbenzene by Freed and Fraenkel.[52] In the case of the 1:4 diydroxydurane cation radical an alteration of line widths is also apparent.[53] These latter cases are at once seen to be apparently similar to the effect observed earlier by Maki,[54] who found that in the cases of the *p*-nitrobenzaldenhyde and the terephthalaldehyde the restricted rotation of the aldehyde group lead to an altered appearance of the hyperfine structure of the spectra. In these cases the ring proton hyperfine coupling constants for the *cis* and *trans* isomers of the *para*-substituted benzene derivatives are influenced by the hindered rotation of the group substituted in the 1 and 4 positions. The linewidth variation observed for the 1:4 dihydroxydurene cation indicates that the methyl proton hyperfine coupling constants are likewise modulated.

For the substituted methyl benzene derivatives like the dinitrodurene anion radical, Freed and Fraenkel[52] assume that the pair of nitro groups undergo a correlated hindered rotation while the methyl groups rotate rapidly. The rotational modulation of $a_N(\phi)$, where $\phi$ is the angle of orientation in the plane of the nitro group with respect to the plane of the benzene ring, causes line broadening by inducing secular and nonsecular relaxation processes determined by the Fourier spectrum of the deviation of the matrix elements of $[a_N(\phi_1)I_1 + a_N(\phi_2)I_2]\cdot S$ from their

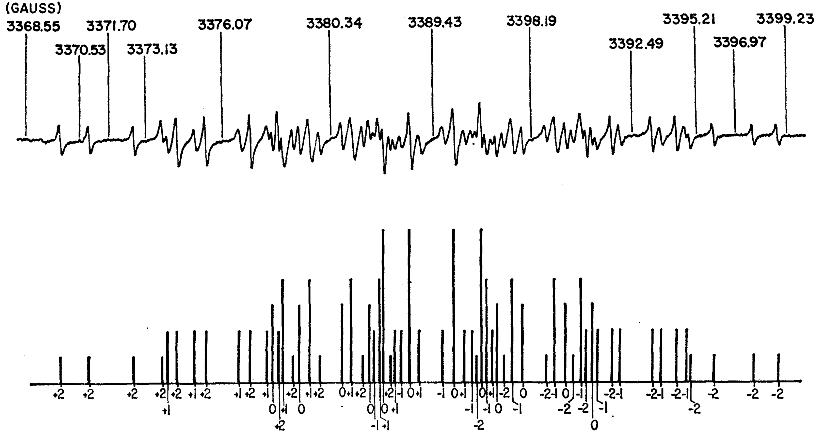

FIG. 7. ESR spectrum of meta dinitrobenzene negative ion. (Fischer and McDowell, reference 51.)

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[49] J. S. Hyde and H. W. Brown, J. Chem. Phys. **37**, 368 (1962).

[50] J. H. Freed, P. H. Rieger, and G. K. Fraenkel, J. Chem. Phys. **37**, 1881 (1962).

[51] P. H. H. Fischer and C. A. McDowell (unpublished).

[52] J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **37**, 1156 (1962).

[53] J. R. Bolton and A. Carrington, Mol. Phys. **5**, 161 (1962).

[54] A. H. Maki, J. Chem. Phys. **35**, 761 (1961).

average value $\langle a_N(\phi)\rangle(I_1 + I_2)\cdot S$. The line shape is Lorentzian and if $J_{11}(0)$ is the secular spectral density for the motion of one nitro group relative to the plane of the ring, it can be shown for $J_{11}(0)$ being large, that the $M_I = 0$ line should be broad, while the $M_I = 0$ line should be so broad that it might not be observed. The amplitudes of the $M_I = \pm 2$ lines and the $M_I = 0$ line would be nearly the same.

The variations in the linewidths observed for hydrocarbon ion radicals are due to relaxation mechanisms which depend on the nuclear spin quantum numbers and which vary as $M$ and $M^2$. There are several theories which have developed to account for these phenomena.[55–58] All, to some extent, derive from the earlier work of Bloembergen, Purcell, and Pound[55] on nuclear relaxation phenomena in liquids. The case of relaxation phenomena in the ESR spectra of free radicals was first examined by McConnell.[54] He showed that if a nuclear spin in the radical had an anisotropic electron hyperfine interaction, then the electron spin is subject to a fluctuation as the radical undergoes Brownian rotation. This time-dependent perturbation induces the electron to reverse its spin and also modulates the frequency of each electron resonance line. It was shown that the width of a line would depend on the nuclear spin quantum numbers of the levels involved in the transition. Kivelson[57] and Stephen and Fraenkel[58] have developed more elaborate theories which, though deriving from McConnell's work, have made use of the ideas developed by Kubo and Tomita.[59] More recently, a somewhat simpler theoretical treatment has been given by Carrington and Longuet-Higgins,[60] and we shall now present an outline of this treatment. Later we show that these theories help to explain the experimental observations on the variations of linewidths which have been mentioned above.

A radical containing one set of equivalent magnetic nuclei can be represented by the Hamiltonian

$$\mathcal{H} = \beta H_\alpha g_{\alpha\beta} S_\alpha + I_\alpha T_{\alpha\beta} S_\alpha \,, \qquad (26)$$

where $I_\alpha$ is the sum of all the nuclears pins in the equivalent set. If there are several magnetic nuclei, even equivalent nuclei, each should strictly be assigned a hyperfine interaction tensor:

$$\mathcal{H} = \beta H_\alpha g_{\alpha\beta} S_\alpha + \textstyle\sum_i I^i_\alpha T^i_{\alpha\beta} S_\alpha \,. \qquad (27)$$

Only if the principal axes of all the $T^i_{\alpha\beta}$ are parallel will (27) reduce to (26). The Hamiltonian $\mathcal{H}$ can be written as the sum of an isotropic term $\mathcal{H}_0$ and a perturbation $\mathcal{H}'$ which depends on the orientation of the radical in the external field. Thus, we write

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \,, \qquad (28)$$

where

$$\mathcal{H}_0 = \beta g H_\alpha S_\alpha + \textstyle\sum_i T^i I^i_\alpha S_\alpha \,. \qquad (29)$$

We have made the substitutions $g = \frac{1}{3}\, g_{\alpha\alpha}$, and $T^i = \frac{1}{3}\, T^i_{\alpha\alpha}$.

We write

$$\mathcal{H}' = \beta H_\alpha g'_{\alpha\beta} S_\beta + \textstyle\sum_i I^i_\alpha t^i_{\alpha\beta} S_\alpha \,; \qquad (30)$$

$g'_{\alpha\beta}$ and $t^i_{\alpha\beta}$ being the anisotropic parts of $g_{\alpha\beta}$ and $T^i_{\alpha\beta}$, namely,

$$g^i_{\alpha\beta} = g_{\alpha\beta} - g\delta_{\alpha\beta}, \quad t^i_{\alpha\beta} = T^i_{\alpha\beta} - T^i\delta_{\alpha\beta} \,. \qquad (31)$$

The eigenstates of $\mathcal{H}_0$ are characterized by the quantum numbers $M_S$ and $M^i_I$, namely, the near eigenvalues of $S_z$ and $I^i_z$, where $z$ is the direction of the external magnetic field.

Since $z$ is the direction of the applied field, $H_x = H_z = 0$, and $I^i_x$ and $I^i_z$ have zero matrix elements between states with the same values of $M^i_I$. Therefore, the matrix elements of $\mathcal{H}'$ within the two states of an observed transition are the same as those of

$$\mathcal{H}'_{zx} + \mathcal{H}'_{zy} + \mathcal{H}'_{zz} \,,$$

where

$$\mathcal{H}'_{zx} = (\beta H_z g'_{zx} + \textstyle\sum I^i_z t^i_{zx}) S_x, \text{ etc.} \qquad (32)$$

The fluctuations in $\mathcal{H}'_{zx}$, etc., may then be associated with the time dependence of the direction cosines $l_{x\alpha}$, etc., between the space-fixed axes and the molecule-fixed axes. With this notation, we have

$$\mathcal{H}'_{zx} = (\beta H_z l_{z\alpha} g'_{\alpha\beta} + \textstyle\sum I^i_z l_{z\alpha} t^i_{\alpha\beta}) l_{\beta x} S_x \,. \qquad (33)$$

The effect of the time-dependent perturbation (33) is first considered. There are off-diagonal elements between the pair of states $|\pm\frac{1}{2}, M^i_I\rangle$; it, therefore, induces transitions between them, but does not modulate their energies. The transition probability depends on the statistical properties of the matrix element

$$X_{(t)} = \langle \tfrac{1}{2}, M^i_I | \mathcal{H}'_{zx} | -\tfrac{1}{2}, M^i_I \rangle \,. \qquad (34)$$

If $X(t)$ has an exponentially decaying autocorrelation function of the type

$$\langle X_{(0)} X_{(t)} \rangle = \langle X^2_{(0)} \rangle \exp\,(-|t|/\tau) \,,$$

by application of the Wiener–Khintchine theorem,

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[55] N. Bloembergen, E. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[56] H. M. McConnell, J. Chem. Phys. **25**, 709 (1956).

[57] D. Kivelson, J. Chem. Phys. **33**, 1094 (1960).

[58] M. J. Stephens and G. K. Fraenkel, J. Chem. Phys. **32**, 1435 (1960).

[59] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[60] A. Carrington and H. C. Longuet-Higgins, Mol. Phys. **5**, 447 (1962).

the probability per unit time of the $X$-induced transition

$|\frac{1}{2},M_I^i\rangle \rightarrow |-\frac{1}{2},M_I^i\rangle$ becomes equal to

$$2\tau\langle X_{(0)}^2\rangle/\hbar(1+\omega^2\tau^2)\,, \tag{35}$$

where $\hbar\omega$ is the energy of the transition. The mean square value of $X_{(0)}$ is given by the equation

$$\begin{aligned}\langle X_{(0)}^2\rangle = {} & (\beta H_z l_{z\alpha} g'_{\alpha\beta} + \sum M_I^i l_{z\alpha} t_{\alpha\beta}^i) \\ & \times l_{\beta x}(\beta H_z l_{z\mu} g'_{\mu\nu} + \sum M_I^i l_{z\mu} t_{\mu\nu}^i) l_{\nu x} \\ & \times \langle \tfrac{1}{2}\,|S_x| - \tfrac{1}{2}\rangle^2\,.\end{aligned} \tag{36}$$

Similar calculations can be made for $\langle Y_{(0)}^2\rangle$ and $\langle Z_{(0)}^2\rangle$. The characteristic lifetime $T_1'$ associated with $X(t)$ and $Y(t)$ together is given by

$$1/T' = \tau P/10\hbar^2(1+\omega^2\tau^2)\,, \tag{37}$$

where $P$ is defined as the tensor invariant

$$P = (\beta H_z g'_{\alpha\beta} + \textstyle\sum_i M_I^i t'_{\alpha\beta})(\beta H_z g'_{\alpha\beta} + \sum_i M_I^i t_{\alpha\beta}^i)\,. \tag{38}$$

The broadening due to $Z(t)$ is given by

$$1/T_2' = 2\tau P/15\hbar^2\,. \tag{39}$$

$P$ can be expanded into three terms. The first is $\beta^2 H_z^2 g'_{\alpha\beta} g'_{\alpha\beta}$ which is independent of the nuclear quantum numbers and is of little interest to us here. Another term in the expansion of $P$ is bilinear in the nuclear quantum numbers $M_I^i$ and is $\sum M_I^i M_I^j t_{\alpha\beta}^i t_{\alpha\beta}^j$. This term is considered later. The remaining cross term

$$2\beta H_z g'_{\alpha\beta} \textstyle\sum_i M_I^i t_{\alpha\beta}^i = 2\beta H_z \sum_i M_I^i g'_{\alpha\beta} T_{\alpha\beta}^i\,. \tag{40}$$

As this is an odd function of the nuclear quantum numbers, this term will affect the two sides of the spectrum in opposite ways. When the radical has sets of equivalent magnetic nuclei, Eq. (40) may be written in the form

$$2\beta H_z \textstyle\sum_i M_I^{(i)}(g'_{\alpha\beta} T_{\alpha\beta}^{(i)})\,, \tag{41}$$

where $M_I^{(i)}$ is the sum of the $M_I$ values for all the nuclei in the set represented by the symbol ($i$), and $T_{\alpha\beta}^{(i)}$ is the hyperfine tensor for *any* nucleus in the set.

Equation (41) shows that if one considers a particular multiplet of lines which differ only in their $M_I^{(i)}$ values, the lines with positive $M_I^{(i)}$ will be broader or narrower than those with negative $M_I^{(i)}$ according to whether their inner product $g'_{\alpha\beta} T_{\alpha\beta}^{(i)}$ is positive or negative.

The above equations agree with those derived by Kivelson[57]; it is, however, to be noted that Kivelson allows for nuclear relaxation in the anisotropic case. Hyde and Brown[49] have interpreted their data on the tetracene cation in sulphuric acid solution in terms of Kivelson's theory. Their arguments are equivalent to saying that because of the difference in the angles of the C–H bonds for classes $a$ and $b$ protons of the tetracene cation (Fig. 6) compared to the class $c$ protons, the sign of the inner products $g'_{\alpha\beta} T_{\alpha\beta}^i$ will be different so that the term linear in $M_I^{(i)}$, Eq. (41), changes sign. This is in agreement with the experimental results. Measurements of the relaxation times $T_1$ and $T_2$ for this system indicates, however, that the data can be fitted to an expression of the form

$$1/T_2 = a + bM_I + cM_I^2\,, \tag{42}$$

which is the relation suggested by the Kivelson theory for the case of one set of equivalent nuclei. The results which deBoer and Mackor[48] obtained for the pyracene cation in sulphuric acid solution obey Eq. (42) very well indeed. In that case, since the isotropic $g$ value for the ion is 2.0025, it is likely that $\delta g$ is small and so the anisotropic dipole–dipole interactions mainly determine the linewidth. Since $\omega\tau_c > 1$, as in the case considered, the broadening effects of the relaxation mechanisms should be proportional to $\tau_c$. Measurement of the linewidth difference between components having the same absolute value of $M_I(\beta)$ (where $\beta$ refers to the four aromatic protons),

TABLE II. Electron spin resonance spectrum of diphenyl nitric oxide.

| | | Half-width at maximum slope | |
|---|---|---|---|
| | | Calc. | Obs. |
| | $M_N = 1$<br>$M_{p,0} = 0$<br>$M_m = 0$ | 0.152 | 0.169 |
| Lower magnetic field side group | $M_N = 1$<br>$M_{p,0} = 1$<br>$M_m = 2$ | 0.764 | ... |
| | $M_N = 1$<br>$M_{p,0} = -1$<br>$M_m = 2$ | 0.751 | ... |
| | $M_N = 0$<br>$M_{p,0} = 0$<br>$M_m = 0$ | 0.107 | 0.122 |
| Central group | $M_N = 0$<br>$M_{p,0} = 1$<br>$M_m = -2$ | 0.408 | ... |
| | $M_N = 0$<br>$M_{p,0} = 1$<br>$M_m = 2$ | 0.553 | ... |
| | $M_N = 1$<br>$M_{p,0} = 0$<br>$M_m = 0$ | 0.242 | 0.203 |
| Higher magnetic field side group | $M_N = -1$<br>$M_{p,0} = -1$<br>$M_m = -2$ | 0.823 | ... |
| | $M_N = -1$<br>$M_{p,0} = -1$<br>$M_m = 2$ | 0.790 | ... |

as a function of the correlation time $\tau_c$ indicated that this expectation was fulfilled.

Deguchi[47] interpreted his results on the ESR spectrum of the diphenyl nitric oxide radical in terms of Kivelson's theory which is, of course, equivalent to the one just outlined. As the spectrum was not completely resolved, Deguchi chose to calculate, from Kivelson's theory, the expected linewidths of the central three lines in each group. Here we may note that recently a better resolved spectrum has been obtained by Pannell.[61] In the case considered, the values available for the $I_z$ component of the nuclear spin of the nitrogen nucleus are 1, 0, $-1$. The six *ortho-* and *para*-protons in the phenyl rings will have $I_z$: $\pm 3$, $\pm 2$, $\pm 1$, 0, and the four *meta*-protons have $I_z$: $\pm 2$, $\pm 1$, 0. For the central three lines in each group, the half-widths calculated at the point of maximum slope are given in Table II. The observed linewidths, where available, are also given and it is seen that good agreement exists between the theoretically calculated values and the experimental results. It is to be noted that Deguchi's spectrum shows that the sharper lines, i.e., those with $M_{I(N)} = +1$ are at the low-field side of the spectrum.

We have already pointed out that the linear equation (41), and the linear term in Eq. (42), implies that the widths of lines with different $M$ values will depend on the sign of $g'_{\alpha\beta}T^{(i)}_{\alpha\beta}$. For nitrogen atoms in aromatic systems there are reasons[58,60] for believing that $g'_{\alpha\beta}T^{(i)}_{\alpha\beta}$ is negative. The lines in the spectrum with positive $M_I$ for the nitrogen atom should be narrower than those lines with negative $M_I$. In the case just discussed, the narrow lines with $M_I = +1$ lie at low field. It follows, therefore, that the isotropic hyperfine splitting constant for the nitrogen atom must be positive. A similar conclusion has been reached for the nitrogen atoms in other aromatic systems.[60,62]

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[61] J. Pannell, Mol. Phys. **5**, 291 (1962).

[62] J. C. M. Henning and C. de Waard, Physica Letters **3**, 139 (1962).

## Discussion on Spin Resonance and Hyperfine Splitting

C. T. O'Konski and L. C. Allen, *Chairmen*

GOODMAN: Why isn't spin-orbit interaction included in the triplet splitting expression?

MCWEENY: It would seem that examination of the $g$ values would be sufficient to show whether or not the spin-orbit coupling was important. The derivation of the spin Hamiltonian shows that the $g$ values involve matrix elements of the spin-orbit operator. When spin-orbit coupling is small the $g$ values are close to 2, and this is the usual case in hydrocarbons; the coupling may then be absorbed into empirical $g$ values and the electron spin–spin coupling calculated quite independently. Only in higher orders of perturbation theory would the spin-orbit coupling lead to spin–spin terms, and one might therefore expect such contributions to be negligible unless the $g$ values differed considerably from the spin-only value.

GOODMAN: It doesn't appear as if all of the spin-orbit interaction is included in the spin–spin Hamiltonian. When the atomic spin-orbit coupling vanishes as in the triplet state of a conjugated hydrocarbon, it is satisfactory to neglect the second-order term, but when there is persistence of atomic spin-orbit interaction (as in ketones, for example) then the interaction between the triplet and singlet probably becomes important to the splitting.

MCWEENY: This comment concerns the general question of how the empirical constants in the spin Hamiltonian can be understood in terms of the electronic wave function. The full Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + (\text{terms involving electron and nuclear spins}) ,$$

where $\mathcal{H}_0$ is a spin-independent electronic Hamiltonian, whose eigenfunctions are made the basis of a perturbation calculation. The remaining terms include interactions between electron and nuclear spins and the magnetic field, spin-orbit coupling, contact couplings, and dipole–dipole couplings. It can then be shown [M. H. L. Pryce, Proc. Phys. Soc. (London) **63**, 25 (1950)] that, to a certain approximation, the eigenvalues of the $\mathcal{H}$ coincide with those of a *spin* Hamiltonian, $\mathcal{H}_{\text{spin}}$, operating within a manifold of electron-nuclear spin states and containing constants which are determined by the electronic wave function. These constants are in fact expressible in terms of the spinless components of certain one- and two-electron density matrices. If we write the transition density matrices between electronic states $\Psi_\kappa$, $\Psi_\lambda$ as