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A Semi-Empirical Approach to the Estimation of ESR Isotropic Hyperfine Coupling Constants in Aromatic Radicals

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Using a generalised product wave function, an expression is given for the isotropic hyperfine coupling constant at a given atom in an aromatic π-radical. By a consistent scheme of approximation the expression is cast in a form in which the coupling constant at a given atom in the radical can be evaluated from the results of a Hückel calculation, provided that certain integrals are known. A scheme for assigning and relating these integrals is given, coupling constants are calculated for ^{13}C, ^{14}N, ^{17}O and ^{19}F atoms, and the calculations compared with experiment.

Bei Verwendung einer Produktwellenfunktion wird ein Ausdruck für die isotrope Hyperfeinkopplungskonstante eines Atomes in einem aromatischen π-Radikal angegeben. Durch ein konsistentes Näherungsschema wird der Ausdruck in eine Form gebracht, bei der die Kopplungskonstante eines Atoms im Radikal aus Resultaten einer Hückelrechnung ausgewertet werden kann, vorausgesetzt, daß gewisse Integrale bekannt sind. Ein Schema, um diese Integrale zu kennzeichnen und miteinander in Beziehung zu setzen, wird angegeben, Kopplungskonstanten werden für ^{13}C, ^{14}N, ^{17}O, und ^{19}F-Atome ausgerechnet und die Rechnungen mit dem Experiment verglichen.

Calcul d'une expression pour la constante de couplage hyperfin isotrope sur un atome dans un radical aromatique π à l'aide d'une fonction d'onde produit généralisé. A l'aide d'un schéma d'approximation cohérent cette expression est mise sous une forme telle que la constante de couplage sur un atome du radical peut être évaluée à partir des résultats d'un calcul de type Hückel, pourvu que certaines intégrales soient connues. On fournit un procédé pour déterminer et relier entre elles ces intégrales; les constantes de couplage pour ^{13}C, ^{14}N, ^{17}O et ^{19}F sont calculées et comparées aux données expérimentales.

Introduction

The theory of ESR isotropic hyperfine coupling constants has been expounded in several ways. For aromatic "π-radicals" the approaches of McConnell [1], of McLachlan *et al.* [2] and of Karplus and Fraenkel [3] are perhaps the best known and most frequently applied.

The aromatic proton splittings of the ESR line, the relationship (1)

$$a^{H} = Q^{H} \varrho^{\pi} \quad (1)$$

is often assumed, where a^H is the proton coupling constant, ϱ^{π} is the "π spin density" (or, more correctly, the square of the coefficient of the $2p$ atomic orbital in the singly occupied π MO) on the carbon atom to which the proton is attached; Q^H is a numerical constant assigned empirically (for most systems, $Q^H = 22-27$ gauss). For ^{13}C and heteroatom splittings, a simple relationship like that for a^H seems inadequate. In such cases, it is common to assume that relationship (2) holds,

$$a^{X} = \mathrm{tr}\, \boldsymbol{Q}^{X} \boldsymbol{\varrho}^{\pi} \quad (2)$$

where contributions from the ϱ^{π} on atom centres adjacent to the heteroatom X, are also considered. So far, it appears that little attempt has been made to relate the Q^X for each system, the values chosen being almost always assigned empirically in such a way as to give closest agreement between the MO calculations of the moment (usually ordinary Hückel calculations) and the observed ESR spectrum.

In the following theory we attempt to develop a new system of relating results of Hückel MO calculations with experiment and at the same time show how the "Q^{X}" for one type of aromatic radical can be both interrelated and also related to the "Q^{X}" for another type (e.g., hydro-carbon radicals vs. heterocyclic radicals).

Theory

Our approach is essentially a development of that proposed by McWeeny and Sutcliffe [4] in which the mechanism through which nuclear spin and unpaired π-electron spin are coupled is accounted for by "spin polarisation" of the underlying σ-electron framework.

Suppose that a given free radical has N electrons (with N odd), in a spin state (S, M). Represent this system by a "generalised product" wavefunction (McWeeny [5]) of strongly orthogonal group functions viz:

$$\Phi_0 = \mathscr{A}\, \Phi_{A,M} \prod_{i=1}^{m} \Phi_{B_b^i} \Phi_{Cc} \tag{3}$$

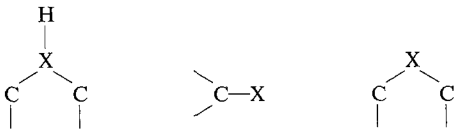
where the group function $\Phi_{A,M}$ describes N_A electrons (N_A odd) and it alone has the spin eigenvalues (S, M). The m functions $\Phi_{B_b^i}$ represent m conventional bonds, each function describing a pair of electrons coupled to a singlet spin state. Φ_{Cc} represents the (inert) core of the molecule and describes an even number (N_c) of electrons in a singlet spin state.

Polarisation of the bonds can be induced by means of configuration interaction with excited state functions in which one bonded group at a time is excited to a triplet state and the functions recoupled to doublets. It has been shown [4] after this configuration interaction the spin density function $Q_1(\boldsymbol{r}, \boldsymbol{r}')$ (to first order) is given by:

$$\begin{aligned} Q_1(\boldsymbol{r}, \boldsymbol{r}') &= Q_1^A(MM|\boldsymbol{r}, \boldsymbol{r}') - 2 \sum_{i=1}^{m} \frac{{}^{\mathrm{H}}\kappa_{B_i^0}}{E(0 \to \kappa_{B_i})} \left(\begin{matrix} S & 1 \\ M & 0 \end{matrix} \middle| \begin{matrix} S \\ M \end{matrix}\right) Q_1^{B_i}(bb_0|\boldsymbol{r}, \boldsymbol{r}') \\ &= Q_1^A(MM|\boldsymbol{r}, \boldsymbol{r}') + \frac{2M}{S} \sum_{i=1}^{m} \frac{k^{B_i A}(bb_0|aa)}{E(0 \to \kappa_{B_i})} Q_1^{B_i}(bb_0|\boldsymbol{r}, \boldsymbol{r}') . \end{aligned} \tag{4}$$

The general definitions of the terms in Eq. (4) are given in [4] and we shall give later the specific forms that they take in this work.

We wish to use the relation (4) to assign spin densities at a centre X which is embedded in various different ways in a conjugated system. Some examples of the kind of embedding that we shall consider are shown symbolically below:



(a) (b) (c)

Fig. 1

We shall be particularly interested in the cases where X is ^{13}C, ^{14}N, ^{17}O, or ^{19}F.

Though we shall not be concerned with performing nonempirical calculations to find $Q_1(r, r')$ we shall specify fairly closely how the group functions are to be constructed in order to show explicitly the detailed form of Eq. (3) and also to indicate the validity of the approximation used.

We imagine a basis set composed of 1*s*, 2*s* and 2*p* Slater type orbitals on every carbon atom and on the atom X (the "heavy" atoms), and a 1*s* orbital on each hydrogen atom. The 2*s* orbitals on the "heavy" atoms are Schmidt orthogonalised against the 1*s* orbitals on the same centre. The basis is then transformed so that the orthogonalised 2*s* orbitals and the 2*p* orbitals on any "heavy" atom are mixed to give sp^2 hybrids lying in the plane of the conjugated system. This transformed basis is then symmetrically orthogonalised so that group functions constructed in this final basis will automatically satisfy the strong orthogonality requirement.

We shall concentrate entirely on conjugated systems in doublet states so that a natural choice for $\Phi_{A,M}$ is then a determinant of MO's doubly occupied so far as possible, with the MO's constructed from the (orthonormal) 2 p_πAO's (that is, those orthogonalised orbitals which are antisymmetric with respect to reflection in the molecular plane). Similarly, Φ_{C_c} will be a determinant of doubly occupied MO's with the MO's constructed from the 1*s* orbitals on the "heavy" atoms.

The group functions $\Phi_{B_b^i}$ for the *i*th bond are constructed from a pair of (orthogonalised) hybrids t_{1i} and t_{2i} which point at one another from the centres at either end of the bond. First a molecular orbital is constructed from these hybrids

$$B_i = C_1^{B_i}\, t_{1i} + C_2^{B_i}\, t_{2i} \tag{5}$$

and the singlet function $\Phi_{B_b^i}$ is constructed as

$$\Phi_{B_b^i}(\boldsymbol{x}_1, \boldsymbol{x}_2) = B_i(\boldsymbol{r}_1)\, B_i(\boldsymbol{r}_2)\, \Theta_{00}(s_1, s_2) \tag{6}$$

where

$$\Theta_{00}(s_1, s_2) = \frac{1}{\sqrt{2}}\,[\alpha(s_1)\,\beta(s_2) - \beta(s_1)\,\alpha(s_2)] \tag{7}$$

where we have used $\boldsymbol{x}$ to denote space and spin variables collectively and $\boldsymbol{r}$ to denote space and s to denote spin variables.

The triplet bond functions $\Theta_{B_{bm}^i} m = 1, 0, -1$ which are needed for the configuration are constructed with the aid of the antibonding partner to B_i viz.

$$\overline{B}_i = C_2^{B_i}\, t_{1i} - C_1^{B_i}\, t_{2i} \tag{8}$$

as:

$$\Phi_{B_{bm}^i}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}}\,[B_i(\boldsymbol{r}_1)\,\overline{B}_i(\boldsymbol{r}_2) - \overline{B}_i(\boldsymbol{r}_1)\,B_i(\boldsymbol{r}_2)]\;\Theta_{1m}(s_1, s_2) \tag{9}$$

with:

$$\begin{aligned} \Theta_{1,1}(s_1, s_2) &= \alpha(s_1)\,\alpha(s_2)\,, \\ \Theta_{1,0}(s_1, s_2) &= [\alpha(s_1)\,\beta(s_2) + \beta(s_1)\,\alpha(s_2)]/\sqrt{2}\,, \\ \Theta_{1,-1}(s_1, s_2) &= \beta(s_1)\,\beta(s_2)\,. \end{aligned} \tag{10}$$

For those group functions involving a "heavy" atom-hydrogen bond, the role of one of the hybrids is played by the 1*s* orbital on the hydrogen.

Using these rules of construction for the group functions, and considering the state $S = M = \frac{1}{2}$, Eq. (4) reduces to:

$$Q_1(\boldsymbol{r}, \boldsymbol{r}') = \pi_o(\boldsymbol{r})\, \pi_o^*(\boldsymbol{r}') + 2 \sum_{i=1}^{m} \frac{\langle \bar{B}_i \pi_o | g | \pi_o B_i \rangle}{E(0 \to \kappa_{B_i})} B_i(\boldsymbol{r})\, \bar{B}_i^*(\boldsymbol{r}') \tag{11}$$

where π_o is the singly occupied MO from $\Phi_{A, \frac{1}{2}}$ and where

$$\langle \bar{B}_i \pi_o | g | \pi_o B_i \rangle = \int B_i^*(\boldsymbol{r}_1)\, \pi_o(\boldsymbol{r}_2) \frac{1}{r_{12}}\, \pi_o(\boldsymbol{r}_1)\, B_i(\boldsymbol{r}_2)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \tag{12a}$$

$$\begin{aligned} E(0 \to \kappa_{B_i}) = {} & \langle \bar{B}_i | \hat{h} | \bar{B}_i \rangle - \langle B_i | \hat{h} | B_i \rangle \\ & + \langle t_{1i} t_{2i} | g | t_{1i} t_{2i} \rangle - \langle t_{1i} t_{2i} | g | t_{2i} t_{1i} \rangle - \langle B_i B_i | g | B_i B_i \rangle \\ & + \langle \pi_o \bar{B}_i | g | \pi_o \bar{B}_i \rangle - \langle \pi_o B_i | g | \pi_o B_i \rangle - \tfrac{3}{2} \langle \pi_o B_i | g | B_i \pi_o \rangle \\ & + \tfrac{1}{2} \langle \pi_o \bar{B}_i | g | \bar{B}_i \pi_o \rangle \\ & + \sum_{\substack{s \neq \pi_o \\ B_i}} \{ 2 [\langle \bar{B}_i s | g | \bar{B}_i s \rangle - \langle B_i s | g | B_i s \rangle] \\ & - [\langle \bar{B}_i s | g | s \bar{B}_i \rangle - \langle B_i s | g | s B_i \rangle] \} \end{aligned} \tag{12b}$$

where in the second sum in (12b) s is one of the B_i.

The operators in these equations are defined by

$$\hat{h} = \frac{\hbar^2}{2m} \nabla^2 - \sum_{n=1}^{N_n} \frac{Z_n e^2}{r_{ni}}, \quad g = \frac{e^2}{r_{12}} \tag{13}$$

where $Z_n e$ is the charge on the nth nucleus.

For spin densities at the point $\boldsymbol{r}_{\mathrm{X}}$ in the nodal plane of the π_o orbitals Eq. (11) reduces to

$$Q_1(\boldsymbol{r}_{\mathrm{X}}) = 2 \sum_{i=1}^{m} \sum_{r,s} c_{ro}^* c_{s2} \frac{\langle \bar{B}_i p_r^\pi | g | p_s^\pi B_i \rangle}{E(0 \to \kappa_{B_i})} \bar{B}_i(\boldsymbol{r}_{\mathrm{X}}) B_i(\boldsymbol{r}_{\mathrm{X}}) \tag{14}$$

where we have formed π_o, by the L.C.A.O. approximation:

$$\pi_o = \sum_r c_{ro} p_r^\pi \,. \tag{15}$$

A straightforward means of normalising the bond orbitals is to write

$$C_1^{B_i} = \cos\theta_i\,, \qquad C_2^{B_i} = \sin\theta_i \tag{16}$$

so that

$$\begin{aligned} \bar{B}_i^*(\boldsymbol{r}_{\mathrm{X}})\, B_i(\boldsymbol{r}_{\mathrm{X}}) = {} & \tfrac{1}{2} \sin 2\theta_i (t_{1i}^2(\boldsymbol{r}_{\mathrm{X}}) - t_{2i}^2(\boldsymbol{r}_{\mathrm{X}})) \\ & - \cos 2\theta_i t_{1i}(\boldsymbol{r}_{\mathrm{X}}) t_{2i}(\boldsymbol{r}_{\mathrm{X}}) \end{aligned} \tag{17}$$

similarly

$$\langle \bar{B}_i p_r^\pi | g | p_s^\pi B_i \rangle = \tfrac{1}{2} \sin\theta_i (\langle t_{1i} p_r^\pi | g | p_s^\pi t_{1i} \rangle - \langle t_{2i} p_r^\pi | g | p_s^\pi t_{2i} \rangle) \tag{18}$$

$E(0 \to \kappa_{B_i})$ is always positive and may be identified approximately with the singlet to triplet excitation energy in the group $\Phi_{B_i^*}$.

In order to put Eq. (14) in a form suitable for semi-empirical calculations we must make certain approximations. The approximations made are set out below, and are consistent with our basic assumptions about the form of the wave function, that is these assumptions are plausible if the molecule is made up of well separated "groups" of bonds, each bond represented by a group function strongly orthogonal to all other group functions.

Approximations

1. We assume that $E(0\rightarrow\kappa_{B_i})$ is the same for all like bonds.

2. We assume that all integrals in the expansion of $\langle B_i\pi_o|g|\pi_o B_i\rangle$ are zero except those of the type

$$\langle t_{1i}p_r^\pi|g|p_r^\pi t_{1i}\rangle \quad \text{and} \quad \langle t_{1i}p_r^\pi|g|p_s^\pi t_{2i}\rangle$$

where p_r^π is on the atom from which t_{1i} originates and p_s^π is on the atom from which t_{2i} originates.

3. For spin density at a site on the ring we assume we need retain only those terms in the sum (14) which refer to bonds adjacent to this site. For a site outside the ring we need retain only the ring-site term in the sum.

4. The number $\bar{B}_i(\boldsymbol{r}_\mathrm{X})\,B_i(\boldsymbol{r}_\mathrm{X})$ is assumed well approximated by $\pm\frac{1}{2}\sin\theta_i t_\mathrm{X}^2(\boldsymbol{r}_\mathrm{X})$, where $t_\mathrm{X}(\boldsymbol{r}_\mathrm{X})$ is the hybrid whose origin is the atom, X, the sign being determined according to whether t_X is t_{1i} or t_{2i}.

Using these approximations in Eq. (14) we can derive the expressions given below for the spin density at the nucleus X, which is related to the isotropic hyperfine coupling constant at X (using conventional notation) by:

$$a^\mathrm{X} = \frac{8\pi}{3} g\beta\gamma_\mathrm{X}\hbar Q_1(\boldsymbol{r}_\mathrm{X}). \tag{19}$$

Proton Splittings

Though we shall not be much concerned with assigning proton coupling constants in conjugated hydrocarbons it is appropriate to show that our scheme can in fact yield the usual McConnell type relation. After a little manipulation it follows from (14) that

$$Q_1(r_\mathrm{H}) = -\frac{|c_{ro}|^2\sin^2 2\theta_\mathrm{CH}}{2E(0\rightarrow\kappa_\mathrm{CH})}\langle t_\mathrm{C}p_r^\pi|g|p_r^\pi t_\mathrm{C}\rangle\,|1s(\boldsymbol{r}_\mathrm{H})|^2 \tag{20}$$

where t_C is the sp^2 hybrid pointing from the rth carbon atom to the adjacent proton, and θ_CH is the angle appropriate to the CH bond (*cf.* Eq. (16)) and $E(0\rightarrow\kappa_\mathrm{CH})$ the C−H bond excitation energy. The exchange integral is positive so that the spin density at the proton $Q_1(r_\mathrm{H})$ must be negative; so the proton coupling constant is given by

$$\begin{aligned} a^\mathrm{H} &= \frac{8\pi}{3} g\beta\gamma_\mathrm{H}\hbar Q(r_\mathrm{H}) \\ &= Q_\mathrm{CH}^\mathrm{H}|c_{r_0}|^2 . \end{aligned} \tag{21}$$

Hence our scheme does yield the familiar McConnell relationship [1]. The validity of this has been extensively investigated, and it is encouraging that the theory reduces to this familiar form for the proton splittings.

We may also easily derive a similar expression for any X – H bond, for example, for a pyrrole-type N – H bond, we obtain:

$$Q_1(r_{\mathrm{H}}) = -\frac{|c_{ro}|^2 \sin^2 2\theta_{\mathrm{NH}}}{2E(0\to\kappa_{\mathrm{NH}})}\langle t_{\mathrm{N}} p_r^\pi | g | p_r^\pi t_{\mathrm{N}}\rangle\, |1s(r_{\mathrm{H}})|^2 \tag{22}$$

Systems in which X is Embedded in the Conjugated System

For all the embeddings of X shown in Fig. 1, it is straight forward to show that the spin density at X must have the following general form.

$$Q_1(r_{\mathrm{X}}) = -A\sum_{r\neq \mathrm{X}} |c_{ro}|^2 + B|c_{\mathrm{X}o}|^2 - C\sum_{r\neq \mathrm{X}} c_{ro}c_{\mathrm{X}o} \tag{23}$$

where the sums run over all nearest-neighbour atoms in the framework. The precise form of the "constants" A, B and C depends on the details of the embedding. For the system shown in Fig. (1a) the constants are

$$\begin{aligned} A &= \frac{\sin^2 2\theta_{\mathrm{XC}}}{2E(0\to\kappa_{\mathrm{XC}})} I_{\mathrm{CC}}\, t_{\mathrm{X}}^2(r_{\mathrm{X}}) \\ B &= \frac{\sin^2 2\theta_{\mathrm{XC}}}{2}\left[\frac{2}{E(0\to\kappa_{\mathrm{XC}})} + \frac{f_{\mathrm{XH}}^2}{E(0\to\kappa_{\mathrm{XH}})}\right] I_{\mathrm{XX}}\, t_{\mathrm{X}}^2(r_{\mathrm{X}}) \\ C &= \frac{\sin 4\theta_{\mathrm{XC}}}{2E(0\to\kappa_{\mathrm{XC}})} I_{\mathrm{XC}}\, t_{\mathrm{X}}^2(r_{\mathrm{X}}), \end{aligned} \tag{24a}$$

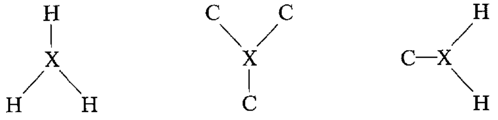
with:

$$\begin{aligned} I_{\mathrm{CC}} &= \langle t_{\mathrm{C}} p_{\mathrm{C}}^\pi | g | p_{\mathrm{C}}^\pi t_{\mathrm{C}}\rangle, & I_{\mathrm{XC}} &= \langle t_{\mathrm{X}} p_{\mathrm{X}}^\pi | g | p_{\mathrm{C}}^\pi t_{\mathrm{C}}\rangle, \\ I_{\mathrm{XX}} &= \langle t_{\mathrm{X}} p_{\mathrm{X}}^\pi | g | p_{\mathrm{X}}^\pi t_{\mathrm{X}}\rangle, & f_{\mathrm{XH}} &= \frac{\sin 2\theta_{\mathrm{XH}}}{\sin 2\theta_{\mathrm{XC}}}. \end{aligned} \tag{24b}$$

For the system shown in Fig. (1b), the constants A and C are just as in Eq. (24a) but

$$B = \frac{\sin^2 2\theta_{\mathrm{XC}}}{2E(0\to\kappa_{\mathrm{XC}})} I_{\mathrm{XX}} t_{\mathrm{X}}^2(r_{\mathrm{X}}). \tag{25}$$

For the system shown in Fig. (1c) the constants are just as for system (1a), on setting the factor f_{XH} to zero.



(a) (b) (c)

Fig. 2

Three other situations which are also of interest and give rise to an equation like (23) for the spin density at X, are indicated symbolically above in Fig. 2. The constants A and C for these systems are just as given in Eq. (24a) but for the system shown in Fig. 2a

$$B = \sin^2 2\theta_{\mathrm{XH}}^2 \, [3 f_{\mathrm{XH}}^2 / E(0 \to \kappa_{\mathrm{XH}})] \, I_{\mathrm{XX}} t_{\mathrm{X}}^2(r_{\mathrm{X}})/2 \qquad (26)$$

while for the system shown in Fig. 2b

$$B = \sin^2 2\theta_{\mathrm{XC}} \, [3 / E(0 \to \kappa_{\mathrm{XC}})] \, I_{\mathrm{XX}} t_{\mathrm{X}}^2(r_{\mathrm{X}})/2 \qquad (27)$$

and for the system shown in Fig. 2c

$$B = \sin^2 2\theta_{\mathrm{XC}} \, [1/E(0 \to \kappa_{\mathrm{XC}}) + 2 f_{\mathrm{XH}}^2 / E(0 \to \kappa_{\mathrm{XH}})] \, I_{\mathrm{XX}} t_{\mathrm{X}}^2(r_{\mathrm{X}})/2 \, . \qquad (28)$$

Calculations

The coefficients c_{r_0} were determined by ordinary Hückel calculations on the molecule considered. In cases where X was a heteroatom, and in consequence parameter values were needed for the Hückel calculations, those given by Streitwieser [6] were chosen.

The integrals I_{CC}, I_{XC}, etc., are regarded as disposable parameters and details of their choice will be discussed later. The remaining parameters necessary were chosen as follows.

1. For a C–C bond we assume that $\theta_{\mathrm{CC}} = 45°$ and for heteropolar bonds θ_{XC} is related to the appropriate valence state σ-orbital electronegativities by the relation

$$\tan \theta_{\mathrm{XY}} = E_{\mathrm{Y}} / E_{\mathrm{X}}$$

where E_{Y} and E_{X} are the Mulliken valence state orbital electronegativities as obtained from the tables by Jaffe and Hinze [7].

2. We identify (see above) $E(0 \to \kappa_{B_i})$ with the singlet-triplet excitation energy of the B_ith bond. In practice, such an excitation would result in spontaneous dissociation of the bond. It therefore seems plausible to assume that $E(0 \to \kappa_{B_i})$ is proportional to or differs by a small amount from the bond dissociation energy for homolysis of ith σ-bond.

3. We assume that $t_{\mathrm{X}}(r_{\mathrm{X}})$ will be proportional to the value the Schmidt orthogonalised (to 1*s*) Slater-type 2*s* and 2*p* orbitals will take at the nucleus X. Thus,

$$t_{\mathrm{X}}^2(r_{\mathrm{X}}) = 2 a_2^5 a_1^6 / \pi (a_1 + \tfrac{1}{2} a_2)^8 \quad \text{u.a.}$$

where a_1 and $a_2/2$ are the appropriate orbital exponents for 1*s*, and 2*s*, 2*p* Slater orbitals, as determined by Slater's rules.

A list of the parameters chosen can be found in Table 1 and the precise values of the Hückel parameters are given with the tables exhibiting the results for heteroatomic systems.

The integral I_{CC} can be assigned from Eq. (20) and (21) and the parameters given in Table 1 if we assume that $|1s(r_{\mathrm{H}})|^2$ is c^2/π a.u., where c is the orbital exponent of the hydrogen orbital. We must also assume that $Q_{\mathrm{CH}}^{\mathrm{H}}$ is known from experiment and we must assign a specific value to c. If we accept a value of 26.8 gauss for $Q_{\mathrm{CH}}^{\mathrm{H}}$ and an orbital exponent of 1.16 (cf. [8]) for c, then we find a value of I_{CC} of 0.3164 eV. There is of course a large measure of freedom in the

Table 1. *Constants and parameters for some magnetic nuclei*

Atom X	γ_X (rad. $\mathrm{sec}^{-1} \cdot \mathrm{gauss}^{-1}$)	Valence state of neutral atom	σ-electronegativity (Mulliken)	$E(0 \rightarrow \kappa_{XC})$ $E(0 \rightarrow \kappa_{XH})$ (eV)	$t^2(r_X)$ (a.u.)	θ_{XC}	θ_{XH}
^{1}H	26753	—	14.34	—	0.4968[a]	—	—
^{13}C	6728	trtrtrπ	17.58	3.609 4.478	0.9549	45°	39.2°
^{14}N pyridine-like	1934	tr^{2}trtrπ	25.74	3.435 —	1.658	34.3°	—
^{14}N pyrrole-like	1934	trtrtrπ^2	24.63	3.435 4.348	1.658	35.5°	30.2°
^{17}O	− 3628	tr^{2}tr^{2}trπ	34.14	3.913 —	2.459	27.2°	—
^{19}F	25179	$s^2p^2p^2p$	24.36	4.783 —	3.712	35.5°	—

[a] With $c = 1.16$, ψ^2 (H1s at $r = 0) = c^3/\pi$ a.u.
Electronegativities from Ref. [7].
γ_X from Ref. [10].
$E(0 \rightarrow K_{XC})$ derived for σ bonded systems from Ref. [11].

choice of c, depending on the precise choice of Q^{H}_{CH}, and the choice made here was to some extent determined by the desire to obtain a value of I_{CC} suitable for use in the calculation of ^{13}C coupling constants.

To evaluate ^{13}C (i.e. in the case where $X = {}^{13}C$) coupling constants I_{CC} is the only integral needed, so assuming that this integral is transferable we can evaluate these coupling constants immediately. In the ^{13}C case $\theta_{XC} = \theta_{CC} = 45°$ and so further simplification of (23) is possible (again irrespective of the precise way in which X is embedded). For the ^{13}C case the constant C vanishes and

$$a^X = -A \sum_{r \neq X} |c_{ro}|^2 + B |c_{Xo}|^2 \tag{29}$$

where now the constants A and B are simply those appropriate to the particular embedding of X (i.e. ^{13}C) multiplied by the appropriate factor as given in Eq. (19). The constants will be quoted in gauss. This equation is completely analogous to the equation of Karplus and Fraenkel [3].

The results of some calculations on ^{13}C splittings are given in Table 2, and it can be seen that they are in extremely good agreement with experiment. For conjugated ring systems there are only two types of embedding likely to be of general interest. The first is when the ^{13}C is a "secondary" carbon (*cf.* Fig. 1a) and in this case

$$A = 16.79 \text{ gauss}, \qquad B = 46.74 \text{ gauss}.$$

The second is when the ^{13}C is a "tertiary" carbon (*cf.* Fig. 2b) in which case

$$A = 16.79 \text{ gauss}, \qquad B = 50.37 \text{ gauss}.$$

To evaluate the coupling constants when X is a heteroatom we need the integrals I_{XX} and I_{XC} to substitute into the general formula for the coupling

Table 2. ^{13}C *splittings*

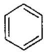
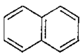
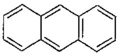
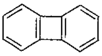
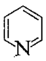
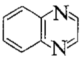
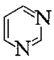
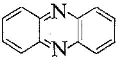
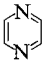
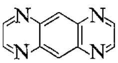
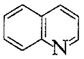
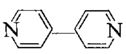
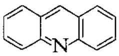
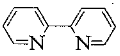
Radical	Position	Calculated a^c (gauss)	Experimental a^c (gauss) anion	cation	Ref.
 benzene		2.197	2.8	—	[12]
 naphthalene	1	7.30	7.3	—	[13]
	2	-0.97	1.0	—	
	9	-6.06	-5.6	—	
 anthracene	9	8.76	8.76	8.48	[14]
	11	-4.58	-4.59	-4.50	
	1	3.57	3.57	—	
	2	-0.177	-0.246	± 0.37	
 biphenylene	1	-2.48	-3.478	-3.20	[15]
	2	$+2.16$	$+2.362$	$+2.48$	
	9	$+1.82$	—	—	
CH_3 methyl		39.48	(neutral radical) $a^c = 38.34$ to 40		[16]

Table 3. ^{14}N *splittings in anion radicals*[a]

Radical	Calculated a^N (gauss)	Experimental a^N (gauss)	Ref.	Radical	Calculated a^N (gauss)	Experimental a^N (gauss)	Ref.
 pyridine	6.985	6.28	[17]	 quinoxaline	5.479	5.64	[20]
 pyrimidine	3.340	3.26	[17]	 phenazine	5.706	5.14	[20]
 pyrazine	7.208	7.22	[17]	 1,4,5,9 tetraza-naphthalene	2.490	2.41	[20]
 quinoline	4.265	3.60	[18]	 4,4′ dipyridyl	3.731	3.64	[20]
 acridine	4.307	3.48	[19]	 2,2′ dipyridyl	3.103	2.54	[21]

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[a] Hückel parameters from Ref. [6]. $h_{\dot{N}} = 0.5$ $k_{CN} = 1.0$.

constant. In the case where X is N, I_{NN} is in principle obtainable from Eq. (22), but unfortunately there does not appear to be the same fund of experimental evidence available for protons in pyrrole like N–H bonds as there is for protons in C–H bonds. We are in similar difficulties with other heteroatoms.

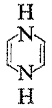
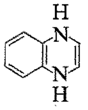
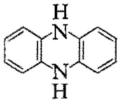
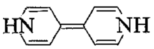
For the nitrogen coupling constants we performed a regression analysis on the data available for "secondary" nitrogens (*cf.* Fig. 1c) in anion radicals and from the best values of A, B and C found, calculated the integrals. The value of I_{NN} was found to be 0.5610 eV while that of I_{NC} was 0.128 eV and the values of the constants were

$$A = 7.63 \text{ gauss}, \quad B = 27.06 \text{ gauss}, \quad C = 2.41 \text{ gauss}.$$

The results for the systems considered are shown in Table 3 and the agreement with experiment is seen to be very good.

There is some experimental data available on nitrogen containing cation radicals where a proton is bonded to the nitrogen. Allowing for the fact that the

Table 4. ^{14}N *and* N-*proton splittings in cation radicals*

Radical	Splittings calculated with various Hückel parameters						Experimental splittings (Ref. [22])	
	a		b		c			
	a^N (gauss)	a^H_{NH} (gauss)[d]	a^N (gauss)	a^H_{NH} (gauss)[d]	a^N (gauss)	a^H_{NH} (gauss)[d]	a^N (gauss)	a^H_{NH} (gauss)
 dihydropyrazine	5.66	−7.58 −6.45	9.86	−11.34 − 9.67	7.30	−8.97 −7.64	7.40	−7.94
 dihydroquinoxaline	5.44	−7.05 −6.01	7.62	− 8.43 − 7.18	6.83	−8.15 −6.95	6.65	−7.17
 dihydrophenazine	5.314	−6.66 −5.68	7.82	− 8.21 − 7.00	6.66	−7.57 −6.45	6.14	−6.49
 dihydro-4,4′ dipyridyl	3.19	−3.69 −3.15	5.17	− 5.68 − 4.84	3.68	−4.79 −4.08	3.56	−4.06

[a] $h_{\ddot{N}} = 1.5$, $k_{CN} = 0.8$, see Ref. [6] (aniline-type nitrogen).

[b] $h_N = 1.5$, $k_{CN} = 1.0$, see Ref. [6] (unprotonated, pyridine-type nitrogen).

[c] $h_{\ddot{N}} = 1.5$, $k_{CN} = 1.0$, $\delta h_N = 0.3$, see Ref. [22].

[d] Upper values calculated with $Q^H_{NH} = -38.64$ gauss (from Eq. (22) H1*s* orbital exponent, $c = 1.16$); lower values calculated with $Q^H_{NH} = -32.95$ gauss (from Eq. (22) H1*s* orbital exponent, $c = 1.10$).

nitrogen in these radicals will be more pyrrole-like and hence have a slightly different electronegativity from the nitrogen in the anion, constants can be calculated from the integrals derived above, appropriate to these cations. The constants are

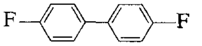
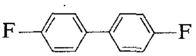
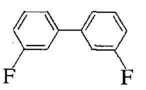
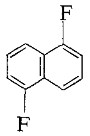
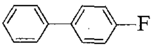
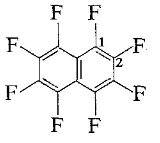
$$A = 7.86 \text{ gauss}, \qquad B = 37.23 \text{ gauss}, \qquad C = 2.19 \text{ gauss}$$

and the results of some calculations are shown in Table 4.

In this table calculations are shown for various values of the Hückel parameters for nitrogen and it can be seen that good agreement with experiment is obtained with accepted pyrrole type nitrogen parameters. In Table 4 we also show some calculated proton coupling constants for the NH proton. It can be seen that better agreement with experiment can be obtained by taking an orbital exponent of 1.1 in the hydrogen 1*s* orbital in this case, rather than the 1.16 found appropriate for a C–H bond.

To evaluate the coupling constants when X is a ^{19}F atom outside the ring (*cf.* Fig. 1b), a regression analysis was again performed on the available experimental data, best values of A, B and C found and from these the integrals I_{FC} and I_{FF} found. Both anions and cations were lumped together for the purposes of the

Table 5. ^{19}F *splittings*[a]

Radical	Calculated a^F (gauss)	Experimental a^F (gauss)	Ref.	Radical	Calculated a^F (gauss)	Experimental a^F (gauss)	Ref.
1. −  4,4′ difluorobiphenyl anion	3.189	3.13	[23]	4. +  4,4′ difluorobiphenyl cation	17.695	19.28	[24]
2. −  3,3′ difluorobiphenyl anion	0.352	0.05 (or 2.04)	[23]	5. +  1,5 difluoronaphthalene cation	17.713	16.98	[24]
3. +  4, fluorobiphenyl cation	19.917	18.59	[24]	6. +  octafluoronaphthalene cation	$a_1^F = 15.825$ $a_2^F = 6.044$	19.0 4.7	[25]

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[a] Hückel parameters (Ref. [6]) $h_{\dot{F}} = 3.0$, $k_{CF} = 0.7$.

regression since the differences in fluorine electronegativity in the two types of system were thought to be negligible. We would not therefore expect vastly different values for the constant.

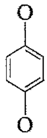
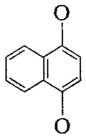
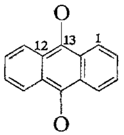
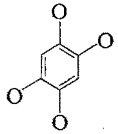
The best constants were:

$$A = 106.2 \text{ gauss}, \qquad B = 684.4 \text{ gauss}, \qquad C = 549.3 \text{ gauss}$$

and the integral values were $I_{FF} = 1.3146$ eV and $I_{FC} = 1.53$ eV.

The results are shown in Table 5. All the available experimental data (with the exception of the compound numbered 6 in the table) were used in the regression analysis. The agreement with experiment is not exceptionally good, but the method seems to be capable of giving reasonable order of magnitude agreements. It was not possible to perform a meaningful regression analysis while compound 6 (the octafluoronaphthalene cation) was included in the data. In view of the probable conformation of this radical this is perhaps not surprising and it is

Table 6. ^{17}O *and* ^{13}C *splittings in semiquinone radicals*[a]

Radical		Position	Calculated a^O (gauss)	Experimental a^O (gauss)	Ref.	Calculated a^C (gauss)	Experimental a^C (gauss)	Ref.
 p-benzosemiquinone	–	0	−11.56	−9.53	[26]			
		1				−6.69	±2.13	[27]
		2				−0.26		
 1,4 naphtho-semiquinone	–	0	− 9.30	−8.58	[26]			
 anthrasemiquinone	–	0	− 7.61	−7.53	[26]			
		1				+0.47	1 or 13, −1.21	
		2				+0.47		[28]
		12				−1.80	−0.47	
		13				−1.83		
 2,5 dioxy-p-benzosemiquinone	3−	0	− 6.65	−4.57	[26]			
		1				−2.63	+2.63	[28]
		3				−4.20	−6.66	

[a] Hückel parameters (Ref. [6]) $h_{\dot{O}} = 1.0$, $k_{CO} = 1.0$.

remarkable that the estimated coupling constants for it come as close as they do to experiment.

Very little experimental evidence is available on oxygen containing heterocycles, and an attempt was made to assign the integrals I_{OO} and I_{OC} from the integral values already obtained.

To find I_{OO} the values of I_{CC} and I_{FF} were plotted as a function of atomic number, a smooth curve drawn through them and a value of I_{OO} interpolated as $I_{OO} = 0.865$ eV. The problem of assigning I_{OC} could not be solved so simply; however it was found that satisfactory agreement with experiment could be obtained by taking $I_{OC} = \sqrt{I_{NC} I_{FC}} = 0.443$ eV. It is difficult to justify this observation in any *a priori* way, but in view of the position of oxygen in the periodic table it seems a plausible assignment.

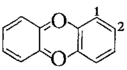
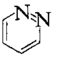
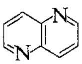
The results of the calculations on some oxygen containing systems are shown in Table 6. The values of the constants for the ^{17}O couplings are

$$A = -14.21 \text{ gauss}, \quad B = -39.04 \text{ gauss}, \quad C = -28.45 \text{ gauss}.$$

Also shown in Table 6 are some ^{13}C coupling constants calculated for a ^{13}C atom in the ring bonded to an ^{17}O atom. We have not so far considered the kind of equation appropriate for the ^{13}C coupling constant in this case, but it is easy to extend the analysis leading to (23) to show that for two atoms X and X′ in this kind of embedding (as in Fig. 1a with X′ replacing H):

$$\begin{aligned} a^{X} = & -A^{XX} \sum_{r \neq X} |c_{ro}|^2 + B^{XX} |c_{Xo}|^2 - C^{XX} \sum_{r \neq X} c_{ro} c_{Xo} \\ & - A^{XX'} |c_{X'o}|^2 + B^{XX'} |c_{Xo}|^2 - C^{XX'} (c_{Xo} c_{X'o}) \end{aligned} \tag{30}$$

Table 7. *Miscellaneous "predictions" on available data*

Radical	X	Calculated a^X (gauss)	Experimental a^X (gauss)	Ref.
[a] +  dibenzdioxin cation	^{13}C	$a_1^C = -2.175$ $a_2^C = +1.760$	$a_1^C = \pm 2.58$ $a_2^C = 1.58$	[29]
[a] −  pyridazine anion	^{14}N	$a^N = 5.601$	$a^N = 5.92$	[21]
[a] −  1,5 diazanaphthalene anion	^{14}N	$a^N = 3.749$	$a^N = 3.37$	[21]

[a] Hückel parameters (Ref. [6]). $h_{\ddot{O}} = 2.0$, $k_{CO} = 0.8$, $h_{\dot{N}} = 0.5$, $k_{CN} = 1.0$.

where the sums run over the carbon atoms adjacent to X in the ring. In the case where $X = {}^{13}C$, C^{XX} vanishes and the constants appropriate to $X = {}^{13}C, X' = {}^{17}O$ are

$$A^{CC} = 16.79 \text{ gauss}, \quad B^{CC} = 33.58 \text{ gauss};$$

$$A^{CO} = 27.94 \text{ gauss}, \quad B^{CO} = 10.17 \text{ gauss}, \quad C^{CO} = -20.21 \text{ gauss}.$$

While the calculated ^{17}O coupling constants shown in Table 6 appear to agree in magnitude and sign with the experimentally observed constants, the agreement for ^{13}C coupling constants is very poor. It is interesting to note, however, that there is one case in which good agreement in absolute magnitude between the observed on calculated constants is obtained, though the calculated sign is opposite to the one assigned experimentally.

Finally, we show in Table 7 some results for systems containing more than one heteroatom in the ring, and for which coupling constants can be predicted using the present theory, and here there seems to be very satisfactory agreement with experiment.

Discussion

It would seem that the theory presented in this paper is capable of unifying fairly adequately a wide range of experimental observations in ESR spectroscopy. It is also capable of almost unlimited extension to other kinds of π-radical, provided that suitable parameter values can be found.

It is recognised that the parametrisation of a scheme like that presented here is, to some extent, arbitrary, but we believe that the parametrisation offered here is physically plausible. Furthermore, there are not so many free parameters in the scheme that the fitting of experimental to calculated results becomes a trivial exercise in curve fitting. The significant fact appears to be that with a plausible choice of a few parameters a large body of experimental data can be unified.

While this paper was in the course of preparation, the paper of Yonezawa *et. al.* [9] appeared in which a theory of similar scope to that given in this paper, was developed. These authors developed the theory in terms of a basic UHF-SCF calculation followed by limited configuration interaction. The theory offered here has the advantage (perhaps slight) of offering the same range of correlations in terms of a somewhat simpler basic calculation.

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