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Virtual Radicals. A Molecular Orbital Study of the Relationship between Some Electron Spin Resonance and Nuclear Magnetic Resonance Spin Coupling Constants[1a]

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Abstract: Within the framework of approximate, self-consistent molecular orbital theory, the restricted Hartree–Fock description of a closed-shell molecule can be taken smoothly into the unrestricted Hartree–Fock description of a radical by placing a nuclear spin perturbation (Fermi contact) of increasing magnitude on a proton. The reasons for this behavior are discussed. The results of semiempirical calculations are used to analyze possible relationships between esr hyperfine splitting constants and nmr nuclear spin coupling constants in H_2 and a few simple hydrocarbons. Comparisons are made with experimental results.

There has been considerable recent interest and activity in the application of approximate self-consistent molecular orbital theory to physical properties of molecules which depend upon electron spin.[2-6] In particular, the intermediate neglect of differential overlap (INDO) method within the unrestricted Hartree–Fock formalism has been fairly successful in correlating calculated spin densities in radicals with observed hyperfine splitting constants assuming a Fermi-contact mechanism.[2] In addition, the INDO method has also been useful in interpreting some nuclear spin coupling constants observed in the nmr spectra of closed-shell molecules, again assuming a Fermi-contact mechanism.[3,4]

Although the hyperfine splitting constants of radicals represent a first-order property, whereas the nuclear spin coupling constants of molecules are second-order properties, several authors have considered the possibility that a close relationship may exist between these two phenomena, primarily because of the appearance of certain terms in common to the quantum mechanical expressions for each property. Thus, McConnell[5] and Karplus[6] have used empirical proton hyperfine splitting constants to estimate the π-electron contribution to proton–proton nuclear spin coupling constants in aromatic and unsaturated systems, and Dixon[7] has suggested that the ratios of certain proton–proton spin coupling constants to proton hyperfine splitting constants should be constant, deviations being entirely due to structural changes in the radical. Recently, Barfield and Karplus have developed a promising approach to partitioning the spin-coupling interaction into distinct contributions, and a relationship with esr couplings is suggested.[8] Barfield and Chakrabarti have recently discussed the role of such relationships in interpreting spin–spin coupling.[9]

The purpose of this paper is to investigate an interesting phenomenon, namely that the closed-shell re-

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(2) (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); (b) *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(3) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2965 (1968).

(4) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1, 11, 4151, 4497, 4506 (1970).

(5) H. M. McConnell, *J. Chem. Phys.*, **30**, 126 (1959).

(6) M. Karplus, *ibid.*, **33**, 1842 (1960).

(7) W. T. Dixon, *Theor. Chim. Acta*, **6**, 359 (1966).

(8) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

(9) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

stricted Hartree–Fock description of a molecule can be taken *smoothly* into the unrestricted Hartree–Fock description of a virtual radical by placing a nuclear spin perturbation (Fermi contact) of increasing magnitude on an atom. If the nuclear spin is placed on a proton, then it turns out that for a given class of approximate molecular orbital methods, the resulting virtual radical is identical, in terms of spin and charge density distribution, to the unrestricted Hartree–Fock description of the real radical formed by the removal of that proton and an electron. A detailed study of this conversion of a molecule into a radical can lead to a better understanding of the relationships between the nuclear spin–spin coupling constants involving a specific proton and the hyperfine splitting constants of the radical formed by the removal of that proton and an electron.

Theory

The theory is attractively simple as it can be developed along somewhat pictorial and intuitive lines. The following development parallels to a certain extent the molecular orbital theory of nuclear spin coupling previously mentioned.[3]

The Fermi contact interaction between an electron and a nuclear spin on atom B is described by the one-electron operator

$$H_{\mathrm{B}}' = (8\pi/3)g\beta\gamma_{\mathrm{B}}h\delta(\mathrm{r}_{\mathrm{B}})I_{z\mathrm{B}}S_z \tag{1}$$

where g, β, λ_{B}, and h are the electron g value (taken as 2.0023), Bohr magneton, nuclear gyromagnetic ratio, and Planck's constant, respectively, and $\delta(\mathrm{r}_{\mathrm{B}})$, $I_{z\mathrm{B}}$, and S_z are the three-dimensional Dirac delta function and the nuclear and electron spin operators, respectively. The variable r_{B} refers to the position of the electron relative to nucleus B. For the isotropic case it is only necessary to consider the z direction for the spin operators, *i.e.*, the direction of quantization of the electron and nuclear spins.

In the presence of a small, positive nuclear magnetic moment there will be a tendency for a doubly occupied molecular orbital ϕ_i (which is assumed not to have a node at nucleus B) to be split into two components, ϕ_i^α and ϕ_i^β, one corresponding to the α electron and the other to the β electron since $\langle\alpha|\,S_z\,|\alpha\rangle = +{}^1/_2$ and $\langle\beta|\,S_z\,|\beta\rangle = -{}^1/_2$. The signs of the above potential terms indicate that the β electron is attracted toward the nucleus B (assuming $I_{z\mathrm{B}}$ is positive) while the α electron is repelled, so that in the presence of the nuclear spin the motions of the two electrons will be correlated. This correlation can be accomodated theoretically by either introducing configuration interaction into the wave function or by allowing the spacial part of ϕ_i to be different for each of the two electrons, *i.e.*, by performing a spin-unrestricted molecular orbital calculation.

If the nuclear spin is small, then the α and β spacial components of ϕ_i will essentially be split evenly so that, to first order, the charge density distribution will be unaffected and the induced spin density (the difference between the α and β charge densities) will be small. As the nuclear magnetic moment is increased, however, there will be a very strong polarization of both the charge and spin density distributions which is somewhat characteristic of radicals. Thus, a closed-shell molecule in the presence of an unrealistically large nuclear magnetic moment might be thought of as a virtual radical.

In general, this artificial virtual radical will have little, if any, physical significance. If, however, the nuclear spin is placed on a proton, then if certain conditions are satisfied in an approximate molecular orbital method, the virtual radical formed will correspond exactly to the unrestricted Hartree–Fock description of the spin and charge density distribution of the real radical formed by the removal of that proton and a single electron. A sufficient condition for this to occur is that, in the limit of infinite nuclear magnetic moment, both the spin and charge of the proton of interest be completely shielded from all electrons but one. In addition to a variety of Hückel-type molecular orbital methods, the INDO method mentioned above satisfies this condition.

In these methods, the molecular orbitals ϕ_i^α and ϕ_i^β are expanded in a basis set of atomic orbitals χ (written as a row vector) which are assumed to be orthonormal

$$\phi_i^\alpha = \chi\mathbf{C}_i^\beta \qquad \phi_i^\beta = \chi\mathbf{C}_i^\beta \tag{2}$$

and

$$\langle\chi|\chi\rangle = 1$$

where $\mathbf{C}_i^\alpha$ and $\mathbf{C}_i^\beta$ are column vectors containing the expansion coefficients. For simplicity, it is also assumed that the proton of interest has associated with it a single 1s atomic orbital χ_{B}.

A description of what occurs in an actual INDO calculation is as follows. As the nuclear magnetic moment of the perturbing proton is made very large, all of the eigenvalues of the Hartree–Fock energy matrix for β electrons are lowered. The lowest of these eigenvalues tends toward $-\infty$, and the remaining β eigenvalues tend toward the eigenvalues of the β energy matrix of the radical. The coefficient of the atomic orbital centered on the perturbing proton becomes unity in the lowest β molecular orbital and becomes zero in the remaining β orbitals, which in turn become identical (aside from an arbitrary phase) with those of the radical. The α orbitals behave in a similar manner, except that the α eigenvalues increase with increasing magnetic moment of the perturbing proton, the highest tending toward $+\infty$ and the remaining tending toward the α eigenvalues of the corresponding radical. Physically, this corresponds to the lowest β electron being "trapped" at the perturbing proton, and the remaining β electrons being completely shielded from this proton by the presence of the trapped β electron. All of the α electrons become shielded from the perturbing proton for large nuclear magnetic moment. This is because the only α orbital with a nonzero coefficient of the 1s atomic orbital of the perturbing proton is the highest, which is vacant.

This type of behavior can be understood formally by considering a simple Hückel-type theory, such as the one used in the theory of nuclear spin coupling constants developed by Pople and Santry.[10] In the presence of the nuclear magnetic moment of the perturbing proton, the Hückel energy matrix can be written as

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(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

$$\det\begin{bmatrix} \epsilon_1{}^{\mathrm{r}} - \lambda & 0 & 0 & \dots & 0 & a_1 \\ 0 & \epsilon_2{}^{\mathrm{r}} - \lambda & 0 & \dots & 0 & a_2 \\ 0 & 0 & \dots & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & \dots & & \epsilon_{m-1}{}^{\mathrm{r}} - \lambda & a_{m-1} \\ a_1 & a_2 & \dots & & a_{m-1} & h_{mm} + x - \lambda \end{bmatrix} = 0 \qquad (9)$$

$$\mathbf{H}(x) = \begin{bmatrix} h_{11} & h_{12} & \dots & h_{1m} \\ h_{21} & h_{22} & \dots & h_{2m} \\ \vdots & & & \vdots \\ h_{m1} & \dots & \dots & h_{mm} + x \end{bmatrix} \qquad (3)$$

with

$$x = \langle \chi_{\mathrm{B}} | H_{\mathrm{B}}' | \chi_{\mathrm{B}} \rangle \qquad (4)$$

where H_{B}' is defined in eq 1. The basis set has been ordered such that χ_{B} is the last element. For $x > 0$ the matrix $\mathbf{H}(x)$ is the Hückel matrix for the α electrons and with $x < 0$ it is the Hückel matrix for the β electrons. It has been assumed that the h_{ij} of eq 3 are independent of H_{B}' so that only the last diagonal element of $\mathbf{H}(x)$ is affected by the perturbation. The Hückel matrix $\mathbf{H}^{\mathrm{r}}$ for the radical formed by the removal of the perturbing proton and an electron is the same as $\mathbf{H}(x)$ except that the last row and column of $\mathbf{H}(x)$ are missing. Thus, $\mathbf{H}(x)$ can be written as

$$\mathbf{H}(x) = \begin{bmatrix} & & h_{1m} \\ \mathbf{H}^{\mathrm{r}} & & h_{2m} \\ & & \vdots \\ h_{m1} & \dots & h_{mm} + x \end{bmatrix} \qquad (5)$$

If $\mathbf{C}^{\mathrm{r}}$ and $\boldsymbol{\epsilon}^{\mathrm{r}}$ are used to denote the eigenvector and (diagonal) eigenvalue matrices of $\mathbf{H}^{\mathrm{r}}$, then $\mathbf{H}(x)$ can be partially diagonalized by the unitary matrix

$$\mathbf{U} = \begin{bmatrix} & & 0 \\ \mathbf{C}^{\mathrm{r}} & & 0 \\ & & \vdots \\ 0 \; 0 & \dots & 1 \end{bmatrix} \qquad (6)$$

such that

$$\mathbf{H}_1(x) = \mathbf{U}^{\dagger}\mathbf{H}(x)\mathbf{U} = \begin{bmatrix} \epsilon_1{}^{\mathrm{r}} & 0 & 0 & \dots & 0 & a_1 \\ 0 & \epsilon_2{}^{\mathrm{r}} & 0 & \dots & 0 & a_2 \\ 0 & 0 & \epsilon_3{}^{\mathrm{r}} & \dots & \dots & a_3 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & \dots & \epsilon_{m-1}{}^{\mathrm{r}} & a_{m-1} \\ a_1 & a_2 & a_3 & \dots & a_{m-1} & h_{mm} + x \end{bmatrix} \qquad (7)$$

where

$$a_i = \sum_{k=1}^{m-1} C_{ki}{}^{\mathrm{r}} h_{km} \qquad (8)$$

Only the last row and column of eq 7 have nonzero off-diagonal elements. Since the roots, λ_j of the secular equation are unaffected by a unitary transformation of $\mathbf{H}(x)$, the characteristic polynomial can be written as shown in eq 9 which can be expanded as

$$(h_{mm} + x - \lambda)Q(\lambda) - \sum_{k=1}^{m-1} a_k{}^2 Q_k(\lambda) = 0 \qquad (10)$$

where

$$Q(\lambda) = \prod_{l=1}^{m-1} (\epsilon_l{}^{\mathrm{r}} - \lambda)$$
$$Q_k(\lambda) = \prod_{l(\neq k)=1}^{m-1} (\epsilon_l{}^{\mathrm{r}} - \lambda) \qquad (11)$$

The problem is now set up in such a way that some useful theorems can be applied. These theorems were proved by MacDonald in an elegant paper discussing the variational principle.[11] The most important point is that the roots λ_i of eq 10 are all separated from one another by the values of $\epsilon_i{}^{\mathrm{r}}$ for *all* values of x (theorem 1 of ref 11)

$$\lambda_1 \leq \epsilon_1{}^{\mathrm{r}} \leq \lambda_2 \leq \epsilon_2{}^{\mathrm{r}} \dots \lambda_{m-1} \leq \epsilon_{m-1}{}^{\mathrm{r}} \leq \lambda_m \qquad (12)$$

where λ_i and $\epsilon_i{}^{\mathrm{r}}$ values are in increasing order. Moreover, if x is chosen such that $x + h_{mm} \geq \epsilon_{m-1}{}^{\mathrm{r}}$ then

$$\lambda_m \geq x + h_{mm} \qquad (13)$$

(corollary 2.1 of ref 11). This is a sufficient condition to ensure that λ_m, the highest eigenvalue of $\mathbf{H}(x)$, goes to infinity as x goes to infinity, and eq 12 ensures that the remaining λ_i's remain finite. For infinite x and finite λ, eq 10 will be satisfied if and only if the first term remains finite, since the second term is always finite for finite λ. This will occur only if $Q(\lambda) = 0$, which is satisfied by $\lambda = \epsilon_i{}^{\mathrm{r}}$. It remains necessary only to show that the matrix $\mathbf{U}$ of eq 6 actually becomes the eigenvector matrix of $\mathbf{H}(x)$ as x goes to infinity. For this, it is sufficient to show only that the eigenvector matrix $\mathbf{V}$ of the matrix $\mathbf{H}_1(x)$ of eq 7 is a unit matrix for infinite x. The eigenvalue equation for the highest column eigenvector $\mathbf{V}_m$ is

$$\mathbf{H}_1(x)\mathbf{V}_m(x) = \lambda\mathbf{V}_m(x) \qquad (14)$$

which is equivalent to the set of linear equations

$$\epsilon_i{}^{\mathrm{r}} V_{im} + a_i V_{mm} = \lambda V_{im} \qquad i = 1, 2, \dots, m - 1 \qquad (15a)$$

$$(h_{mm} + x)V_{mm} + \sum_{k=1}^{m-1} a_k V_{km} = \lambda V_{mm} \qquad (15b)$$

The normalization requirement is

$$\sum_{k=1}^{m} V_{km}{}^2 = 1 \qquad (16)$$

so that it is sufficient to show that $V_{im} = 0$ $(i \neq m)$ as x becomes infinitely large. Equation 15a can be re-

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(11) J. K. L. MacDonald, *Phys. Rev.*, **43**, 830 (1933). MacDonald has assumed, as we have, that there are no degeneracies among the eigenvalues. The theorems, however, remain valid for symmetry-induced degeneracies.

written as

$$|V_{im}| = \frac{|a_i||V_{mm}|}{|\lambda - \epsilon_i^{\mathrm{r}}|} \leq \frac{|a_i|}{|\lambda - \epsilon_i^{\mathrm{r}}|} \leq \frac{|a_i|}{|h_{mm} + x - \epsilon_i^{\mathrm{r}}|} \quad (17)$$

where the first inequality is from eq 16 and the second from eq 13. In the limit of infinitely large x, the last term on the right vanishes, so that all of the V_{im}'s vanish except for V_{mm}, which becomes unity (aside from a phase) because of the normalization requirement. Since the remaining eigenvectors $\mathbf{V}_k$ ($k \neq m$) are orthogonal to $\mathbf{V}_m$, the coefficients V_{mk} are all zero. The first $m - 1$ rows and columns of $\mathbf{V}$ thus represent a matrix which is the eigenvector matrix of the diagonal matrix of the ϵ_i^{r}'s ($i = 1, m - 1$). Since the eigenvector matrix of a diagonal matrix is the unit matrix the matrix $\mathbf{V}$ must be a unit matrix.

Exactly parallel arguments can be used to show that as x goes to $-\infty$, the lowest eigenvalue of $\mathbf{H}(x)$ goes to $-\infty$, while the remaining eigenvalues and eigenvectors become those of $\mathbf{H}^{\mathrm{r}}$. In this case, eq 13 is replaced by

$$\lambda_1 \leq x + h_{mm}$$

when x is chosen such that $x + h_{mm} \leq \epsilon_1^{\mathrm{r}}$.

The situation is similar for the INDO method, although it is complicated by the fact that the α and β molecular orbitals can no longer be treated independently since they are coupled through the electron repulsion terms. As in the Hückel case, the effect of the infinite nuclear spin of the proton is isolated from the rest of the molecule by this omission of terms of the form $\langle \chi_i | \delta(\mathbf{r}_{\mathrm{B}}) | \chi_j \rangle$, where both χ_i and χ_j are not χ_{B}. This approximation has been made in all previous applications of the INDO method, both to hyperfine splitting constants of radicals and to nmr coupling constants of singlet molecules.

As indicated above, occurrence of a virtual radical in a calculation requires the satisfaction of the condition of complete charge and spin isolation of the proton with infinite magnetic moment. In order that the charge of the proton be completely isolated from the rest of the molecule for an infinite Fermi-contact interaction, it is necessary that the electron trapped at the proton completely shield this nuclear charge from the remaining electrons. In *ab initio* methods this could only be accomplished by optimizing the exponent of the 1s basis function of the proton to allow this basis function to collapse to a point at the nucleus. In the INDO method, this step is not necessary since penetration terms are formally set equal to zero (this was not true in the original CNDO/1 method[12]). In other words, the Coulomb attraction of the other electrons to the proton is exactly canceled by the repulsion of these electrons by the electron trapped at the proton. Formally, in the INDO theory, this is equivalent to the relation

$$\left\langle \chi_i \left| \frac{1}{r_{\mathrm{B}}} \right| \chi_i \right\rangle = \left\langle \chi_i(1)\chi_{\mathrm{B}}(2) \left| \frac{1}{r_{12}} \right| \chi_i(1)\chi_{\mathrm{B}}(2) \right\rangle \quad (18)$$

In the INDO theory of radicals, the hyperfine coupling constant at nucleus A is given by

$$\alpha_{\mathrm{A}} = (4\pi/3)g\beta h\gamma_{\mathrm{A}}\langle S\rangle^{-1}s_{\mathrm{A}}^{2}(0)\rho_{\mathrm{s_A}} \quad (19)$$

where $s_{\mathrm{A}}^{2}(0)$ is a parameter that represents the value of the square of the valence s atomic orbital at nucleus A and $\rho_{\mathrm{s_A}}$ is the diagonal element of the spin-density matrix corresponding to this orbital. In the theory of nuclear spin coupling constants, the expression used for the coupling constant is

$$J_{\mathrm{AB}} = \left(\frac{4\pi}{3}g\beta h\right)^2 \gamma_{\mathrm{A}}\gamma_{\mathrm{B}}s_{\mathrm{A}}^{2}(0)\left(\frac{\partial \rho_{\mathrm{s_A}}}{\partial h_{\mathrm{B}}}\right)_{h_{\mathrm{B}}=0} \quad (20)$$

where

$$h_{\mathrm{B}} = (4\pi/3)g\beta h\gamma_{\mathrm{B}}s_{\mathrm{B}}^{2}(0)I_{z_{\mathrm{B}}} \quad (21)$$

Thus plotting diagonal s-orbital spin-density matrix elements for various atoms in a molecule *vs.* the Fermi contact interaction at proton B should give a family of curves, the slopes at the origin being proportional to the nuclear spin coupling constants of the molecule and the asymptotic values being proportional to the hyperfine splitting constants of the radical formed by the removal of the hydrogen atom B. The demonstration of this family of curves should lend support to previous assumptions or alternate theoretical developments of relationships between nmr spin coupling constants and esr hyperfine splitting constants.

Calculations and Discussion

INDO calculations were carried out on the molecules hydrogen, acetylene, ethylene, propene, butadiene, and benzene and on their corresponding radicals. These cases were chosen because relatively little structural change would be expected to occur in the formation of the radical by removal of a hydrogen atom. Standard geometries[13] were used in the calculations. For each molecule, the perturbation h_{B} was varied in powers of 10 from 10^{-4} through 10^{3} atomic units (hartrees). Additional points were calculated in the region of large curvature. For the largest value of the perturbation, the computed spin densities reproduced those calculated for the corresponding radicals to within about 10^{-4}.

Hydrogen. The hydrogen molecule is generally trivial and uninteresting from the standpoint of an INDO calculation (which is identical with CNDO/2 in this case), the calculated nuclear spin coupling constant being in poor quantitative agreement with the experimental value.[3] Nevertheless, it is of academic interest since it can be solved in closed form and since the shape of the curve of $\rho_{\mathrm{s_A}}$ *vs.* h_{B} closely resembles the curves for the other molecules studied. Since H_2 dissociates into two hydrogen atoms, the total charge density on each atom should be unity. The spacial parts of the molecular orbitals then take on the form

$$\begin{aligned} \phi^{\alpha} &= \sin\theta(\mathrm{a}) + \cos\theta(\mathrm{b}) \\ \phi^{\beta} &= \cos\theta(\mathrm{a}) + \sin\theta(\mathrm{b}) \end{aligned} \quad (22)$$

where a and b represent 1s atomic orbitals centered on protons A and B, respectively. The restricted solution is obtained at $\theta = \pi/4$ when the nuclear spin is zero. In the presence of the Fermi contact interaction, the expression for the electronic energy becomes

$$E = 2\langle \mathrm{a}|h|\mathrm{a}\rangle + 2\zeta\sin 2\theta + x_{\mathrm{B}}\cos 2\theta + \gamma_{\mathrm{AB}} + \frac{1}{2}\sin^2 2\theta[\gamma_{\mathrm{AA}} - \gamma_{\mathrm{AB}}] \quad (23)$$

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(12) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(13) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table I. Calculated and Experimental Data for Ethylene and Vinyl Radical

Atom	Calculated						Experimental		
	Initial slope	Asymptote[a]	Ratio[b]	J^c	α^d	J/α^e	J^f	α^g	J/α
C^α	0.547	0.207	2.6	156.7	178.0	0.86	156.4	107.57	1.45
C^β	−0.040	−0.018	2.2	−11.6	−15.4	0.73	−2.4	−8.35	0.29
H_{gem}	0.031	0.032	1.0	3.2	13.9	0.24	2.5	13.4	0.19
H_{cis}	0.089	0.047	1.9	9.3	20.4	0.46	11.7	37.0	0.32
H_{trans}	0.239	0.127	1.9	25.2	55.1	0.46	19.1	65.0	0.29

[a] Values taken from Figure 2. [b] Ratio of slope to asymptote. [c] Values in hertz calculated according to eq 20, using the $s_A{}^2(0)$ values given in ref 3. [d] Values in gauss calculated according to eq 20, using the $s^2{}_A(0)$ values given in ref 2b. [e] Values calculated as the ratios of entries in previous two columns. [f] Values in hertz, taken from ref 3. [g] Values in gauss, taken from ref 3.

where

$$\langle a|h|a\rangle = -\frac{1}{2}(I + A)_s - \frac{1}{2}\gamma_{AA}$$

$$\zeta = \beta_H{}^0\langle a|b\rangle \tag{24}$$

$$\gamma_{AB} = \left\langle a(1)b(2)\left|\frac{1}{r_{12}}\right|a(1)b(2)\right\rangle$$

Following the usual INDO formulation, the parameters $(1/2)(I + A)_s$ and $\beta_H{}^0$ are assigned values of 7.1761 and −9.0 eV, respectively. The new independent variable x_B is defined as $\langle a|H_B'|a\rangle$ for convenience.

The stationary condition is

$$\frac{dE}{d\theta} = 0 = 4\zeta \cos 2\theta - 2x_B \sin 2\theta + 2 \sin 2\theta \cos 2\theta(\gamma_{AA} - \gamma_{AB}) \tag{25}$$

It is easily verified that the diagonal s-orbital element of the spin-density matrix at atom A is given as $\rho_{s_A} = -\cos 2\theta$. From eq 25, the curve of ρ_{s_A} *vs.* x_B is then determined as one of the roots of a quartic equation. At the normal equilibrium geometry, the term $\lambda_{AA} - \lambda_{AB}$ is small relative to ζ so that in this case there are two real distinct roots of eq 25, one corresponding to a maximum energy and the other corresponding to a minimum. The curves ρ_{s_A} *vs.* x_B for these roots are plotted in Figure 1, the upper curve corresponding to the minimum energy. Implicit differentiation of eq 25 gives the slope at the origin as

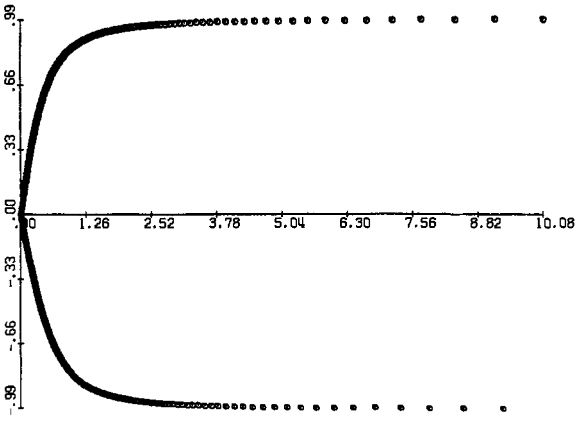


Figure 1. Plot of s-orbital spin density (ordinate) *vs.* h_B in hydrogen. The upper curve corresponds to the minimum-energy solution to ref 25 and the lower curve corresponds to the maximum-energy solution.

$$(\partial\rho_{s_A}/\partial x_B)_0 = -1/(\gamma_{AA} - \gamma_{AB} \pm \zeta) \tag{26}$$

which corresponds to the asymptotic value, $\rho_{s_A}(\infty) = \pm 1$. Equation 26 gives rise to the rather large calculated nuclear spin coupling constant of J_{HH} = 408 Hz.[3] The curve in Figure 1 then represents a monotonic function relating a large slope at the origin to a large (for radicals) asymptotic value. It is interesting to note, however, that the asymptotic value is independent of all parameters concerning the perturbed proton, such as the bond length, whereas, from eq 26. the initial slope will vary with such parameters.

Ethylene. The curves of diagonal s-orbital spin-density matrix elements *vs.* h_B for ethylene are shown in Figure 2. Aside from a slight maximum in the curve for the carbon atom directly bonded to the perturbed proton, the curves are all monotonic and resemble quite closely the shape of the curves in Figure 1 for hydrogen. Moreover, the curves do not intersect (except, of course, at the origin), which implies a rough proportionality between the slope and asymptote of each curve.

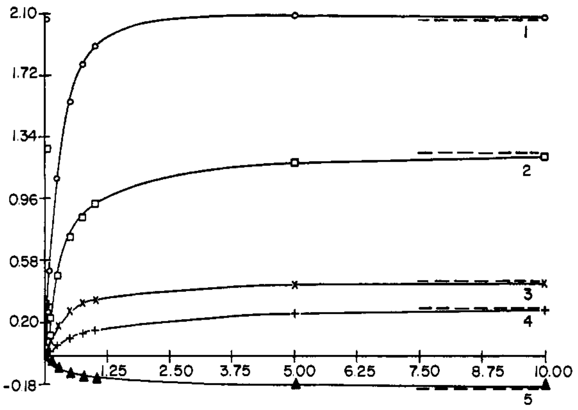


Figure 2. Plot of valence s-orbital spin densities (ordinate/10) of different atoms in ethylene *vs.* h_B. The curves refer to (1) carbon directly bonded to B, (2) vicinal proton trans to B, (3) vicinal proton cis to B, (4) geminal proton, (5) geminal carbon. The points marked on the ordinate axis represent the asymptotic values which are also indicated by the dashed lines.

The relevant data for ethylene and the vinyl radical are collected in Table I. The first three columns represent the data from Figure 2, whereas the last three are experimental data taken from the literature.[2b,3] The slopes at the origin were estimated by a finite difference technique.[3] The relative similarity of the ratios in the third column is striking. This together with the smooth, monotonic behavior of the curves in Figure 2 seem to indicate that essentially the same mechanism is operative in determining the hyperfine splitting constant and the corresponding nuclear spin coupling constant. For example, the fact that the sp^2 hybrid orbitals on the carbon atom have a larger overlap in the trans configuration than in the cis is used to rationalize the relative magnitudes of the cis and trans vicinal spin coupling constants in ethylene. The same argument would be used to explain the relative magnitudes of the hyperfine splitting constants of the protons trans and cis to the radical site in the vinyl radical.

The calculated data of the first three columns of Table I cannot be compared directly with the experimental magnetic resonance parameters in the last three columns because of the difference in units. From eq 19 and 20 the ratio J_{AB}/α_A is given by

$$\frac{J_{AB}}{\alpha_A} = \frac{4\pi}{3} g\beta h\langle S\rangle\gamma_B {s_B}^2(0)\left(\frac{\rho_{sA}}{\partial h_B}\right)_0 / \rho_{sA}(\infty) \qquad (27)$$

All of the quantities in the above equation are either universal constants or computed in the INDO calculation except ${s_B}^2(0)$, the value for the square of the valence s orbital at the nucleus B. This atomic parameter was assigned different values depending on whether the theory was applied to molecules or radicals, the value for nuclear spin coupling constants in molecules being 4.0318 for carbon and 0.3724 for hydrogen, whereas 2.042 and 0.338 were used for the corresponding values in the theory of hyperfine splitting in radicals. The present treatment indicates that since the two cases represent essentially the same interactions, it would have been more consistent to choose ${s_B}^2(0)$ to be the same in both cases. Rather than reevaluate this parameter by considering both the esr and nmr data together, various ratios of the entries in Table I will be used to compare the calculations with experiment. For completeness, we have included in the table calculated values of J's and α's and their ratios, using the above reported ${s_A}^2(0)$ values.

In the case of the protons, the pattern of the results is remarkably well reproduced. Thus the calculated ratio of slope/asymptote for the geminal case is somewhat smaller than that for the two vicinal protons, which are about the same. This is also the case for the experimental ratios.

The case for the carbons is somewhat different. Although the INDO method predicts similar ratios for both the α and β carbons, the experimental ratios differ by a factor of 5. However, it should be noted that the worst correlation between the nuclear spin coupling constant and hyperfine splitting constant should be for the case in which the atom is directly bonded to the perturbing proton. The reason for this is that the nuclear spin coupling constants between directly bonded atoms will be dominated by terms related to the perturbing proton, such as bond length. The hyperfine splitting constant of the α carbon will, on the other hand, be independent of such effects, and such effects will be masked to a large extent for the longer range coupling constants.

It should be noted that geometrical alterations within the radical framework, by which it deviates from the structure of the parent hydrocarbon by more than just removal of a hydrogen atom, are not taken into account in these calculations. Such alterations may in part be responsible for some features of disparity between calculated and experimental results.

Acetylene. The results for acetylene and ethynyl radical are collected in Table II. The curves of s-orbital spin density *vs.* h_B are virtually the same in shape as those for ethylene, so they are neither reproduced nor discussed here. The hyperfine splitting constants for the carbon atoms in the ethynl radical have not been measured, although the value for the proton is 16.1 G. The experimental nuclear spin coupling constants are +248.7, +49.3, and 9.5 Hz for the α and β carbons and the vicinal proton, respectively.

Table II. Calculated Initial Slopes and Asymptotic Values of ρ_{sA} for Acetylene at Three Carbon–Carbon Bond Lengths

R_{CC}, au	Atom	Initial slope	Asymptote	Ratio	J	α	J/α
2.08	C^α	0.739	0.313	2.4	211.4	269.2	0.79
	C^β	0.006	0.002	3.0	1.7	1.7	1.00
	H	0.138	0.088	1.5	14.5	38.2	0.36
2.18	C^α	0.780	0.335	2.3	223.1	288.1	0.76
	C^β	0.008	0.004	2.0	2.3	3.4	0.66
	H	0.117	0.074	1.6	12.3	32.1	0.38
2.28	C^α	0.818	0.335	2.4	233.9	288.1	0.79
	C^β	0.009	0.005	1.8	2.6	4.3	0.59
	H	0.103	0.065	1.5	10.8	28.2	0.36

The ratios of initial slope to asymptotic value for the three atoms behave in much the same way as in ethylene, all being of the same order of magnitude, and the C^α ratio being slightly larger than that for C^β, while the ratio for the vicinal proton is roughly the same as for the vicinal protons in ethylene. An anomaly exists, however, in the nuclear spin coupling constants between the proton and the carbon atoms. Experimentally, $J_{C^\alpha H}$ is about five times as large as $J_{C^\beta H}$, both values being positive. The INDO theory predicts this ratio to be about 100, the $J_{C^\beta H}$ value obtained being over an order of magnitude smaller than the experimental value.[3] Although the experimental values are not known, the same large ratio of the asymptotic values for C^α and C^β is also predicted by the INDO theory.

The calculations were performed at different C–C bond lengths to study this effect on the results. From Table II, it is seen that each initial slope changes in the same way as the asymptotic values, so that the ratios remain relatively constant as R_{C-C} is varied over a small range. This again supports the hypothesis that, in the INDO theory, the same mechanisms are in effect for both the nmr and esr results.

Benzene. The results for benzene and phenyl radical are given in Table III. Again the calculated ratios are more or less constant, even when obtained from very small numbers. Also, as was the case with ethylene and acetylene, the most serious discrepancies between the calculated and experimental values occur with carbon atoms, the wrong sign being predicted for the small coupling constant for the β carbon. It is unfortunate that the hyperfine splitting constants for the carbon atoms in the phenyl radical are unknown The order of the ratios for the ortho and meta protons is predicted correctly, however.

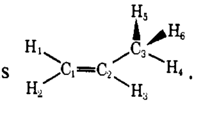
Propene and Butadiene. Propene and butadiene deserve special attention since each contains nonequivalent hydrogens; *i.e.*, it is possible to produce more

Table III. Calculated and Experimental Data for Benzene

Atom	Calculated						Experimental		
	Initial slope	Asymptote	Ratio	J	α	J/α	J	α	J/α
C^{α}	0.490	0.185	2.6	140.3	159.1	0.85	157.5		
C^{β}	−0.017	−0.006	2.8	−4.9	−5.2	0.92	1.0		
C^{γ}	0.033	0.013	2.6	9.4	11.2	0.85	7.4		
C^{δ}	−0.008	−0.003	2.7	−2.3	−2.6	0.89	−1.1		
H_{ortho}	0.077	0.035	2.2	8.1	15.2	0.53	7.54	19.5	0.39
H_{meta}	0.021	0.011	1.9	2.2	4.7	0.46	1.37	6.5	0.21
H_{para}	0.017	0.007	2.4	1.1	3.0	0.58	0.69		

Table IV. Calculated Initial Slopes and Asymptotic Values of ρ_{sA} for Propene[a]

Perturbed atom		Coupled atom								
		C_1	C_2	C_3	H_1	H_2	H_3	H_4	H_5, H_6	Av ($H_4H_5H_6$)
H_1	Initial slope	0.562	−0.035	0.020	*	0.046	0.248	−0.007	−0.025	−0.019
	Asymptote	0.212	−0.015	0.010	*	0.040	0.130	−0.004	−0.010	−0.008
	Ratio	2.6	2.3	2.0	*	1.2	1.9	1.7	2.5	2.4
H_2	Initial slope	0.534	−0.034	0.041	0.045	*	0.091	0.018	−0.027	−0.012
	Asymptote	0.204	−0.014	0.020	0.037	*	0.045	0.010	−0.011	−0.004
	Ratio	2.6	2.4	2.1	1.2	*	2.0	1.8	2.5	3.0
H_3	Initial slope	−0.039	0.526	−0.010	0.249	0.091	*	0.066	0.066	0.071
	Asymptote	−0.045	0.193	−0.002	0.121	0.043	*	0.037	0.029	0.032
	Ratio	2.6	2.7	5.0	2.1	2.1	*	2.2	2.3	2.2

[a] The numbering convention is  .

than one σ-type radical by removing different hydrogens. Also, in contrast to the previous molecules, each of these molecules contains a C–C single bond.

The calculated results are shown in Tables IV and VI, whereas the known experimental results are in Tables V and VII. An asterisk is used to denote the perturbed proton for each case. The curves of s-orbital spin density *vs.* h_B for these molecules are not given here, as they are the same as those for all the other molecules studied in that they are all smooth, monotonic functions which do not cross and which have initial slopes that are roughly proportional to the asymptotic values.

Table V. Experimental Nuclear Spin Coupling Constants J (Hz) and Hyperfine Splitting Constants α (G) for Propene[a]

Perturbed atom		Coupled atom			
		H_1	H_2	H_3	H_{Me}
H_1	J	*	2.1^b	16.8^b	-1.8^b
	α	*			
	J/α	*			
H_2	J	2.1^b	*	10.0^b	-1.3^b
	α		*		
	J/α		*		
H_3	J	16.8^b	10.0^b	*	6.4^b
	α	58.9^c	32.9^c	*	19.5^c
	J/α	0.28	0.30	*	0.34

[a] The atom numbering convention is the same as in Table IV. [b] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961). [c] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

Although the ratios of initial slopes to asymptotic values are not constant, it is interesting to note that the ratio for the geminal proton is smaller than the ratios for the vicinal protons in both propene and butadiene, in agreement with the experimental order for propene (the experimental ratios for butadiene are not presently known). This is the same situation as previously noted for ethylene. Moreover, an examination of Tables I–IV and VI reveals that the calculated ratios for all geminal protons occur in the range between 1.0 and 1.4, whereas the vicinal case has ratios which occur between 1.9 and 2.3, except for acetylene with its ratio of 1.6. The ratios for the longer range protons are less reliable because of the small magnitudes of the numbers involved, but these tend to be more or less similar in magnitude to the ratios for the vicinal protons. A possible explanation for this phenomenon might be that a "direct interaction" with the perturbing proton would be different for geminal and vicinal protons. This "direct interaction" might be defined as the contribution to the nmr spin coupling constant from terms which *do not* contribute to the esr hyperfine splitting constant. In the Hückel method, these terms would be be the off-diagonal elements of the right-hand side of eq 7. If these terms should behave in such a way as to make the geminal coupling constant smaller in magnitude than it would be if calculated without these terms and/or the vicinal coupling constant larger, then this would account for the ratios of slope/asymptote for the geminal cases being smaller than those for the vicinal cases. Moreover, if this "direct interaction" contribution should diminish in magnitude with increasing distance from the perturbing proton, then the ratios for the longer range protons would be expected to be closer to those for vicinal protons than to those for geminal protons, as seems to be the case for the INDO calculations.

The results indicate that the initial slope might be approximately related to the asymptotic value in the following way

Table VI. Calculated Initial Slopes and Asymptotic Values of ρ_{sA} for Butadiene[a]

Perturbed atom		Coupled atom									
		C_1	C_2	C_3	C_4	H_1	H_2	H_3	H_4	H_5	H_6
H_1	Initial slope	0.564	−0.032	0.023	−0.006	*	0.051	0.237	−0.010	0.006	0.004
	Asymptote	0.215	−0.016	0.013	−0.004	*	0.041	0.127	−0.006	0.004	0.003
	Ratio	2.6	2.0	1.8	1.5	*	1.2	1.9	1.6	1.5	1.3
H_2	Initial slope	0.515	−0.029	0.047	−0.002	0.051	*	0.083	−0.009	0.019	0.006
	Asymptote	0.198	−0.014	0.024	−0.002	0.037	*	0.041	−0.006	0.012	0.004
	Ratio	2.6	2.1	2.0	1.0	1.4	*	2.0	1.5	1.5	1.5
H_3	Initial slope	−0.032	0.537	−0.010	−0.009	0.237	0.083	*	0.163	−0.009	−0.010
	Asymptote	−0.015	0.200	−0.004	−0.005	0.118	0.040	*	0.078	−0.005	−0.005
	Ratio	2.2	2.7	2.5	1.7	2.0	2.1	*	2.1	1.7	2.0

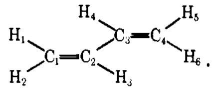
[a] The numbering convention is .

Table VII. Experimental Nuclear Spin Coupling Constants J (Hz) for Butadiene[a]

Perturbed atom	Coupled atom					
	H_1	H_2	H_3	H_4	H_5	H_6
H_1	*	1.74	17.05	−0.83	0.60	0.69
H_2	1.74	*	10.17	−0.86	1.30	0.60
H_3	17.05	10.17	*	10.41	−0.86	−0.83

[a] R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964). The atom numbering convention is the same as in Table VI.

$$\rho_{sA}(\infty) \approx F([\partial \rho_{sA}/\partial h_B]_0) \tag{28}$$

where the function F depends on the particular molecule and the type of interaction (*i.e.*, geminal, trans-vicinal across a double bond, etc.). The Hellmann–Feynman theorem implies that[14]

$$(\partial \rho_{sA}/\partial h_B)_0 = (\partial \rho_{sB}/\partial h_A)_0 \tag{29}$$

so that, according to eq 28

$$\rho_{sA}(h_B = \infty) \approx \rho_{sB}(h_A = \infty) \tag{30}$$

Equation 30 would hold even for nonequivalent protons. An examination of Tables IV and VI supports this hypothesis for the calculated results. Thus, for the proton geminal to the radical site in the two radicals formed by removing the hydrogen cis and trans to the methyl group in propene the calculated spin densities are 0.040 and 0.037, respectively. For the two vicinal cases, the spin densities are 0.130 and 0.121, and 0.045 and 0.043 for the trans and cis cases, respectively. In butadiene, the geminal hydrogen spin densities are 0.041 and 0.037 for radical sites cis and trans to the vinyl group, and the vicinal spin densities are 0.127 and 0.118 and 0.041 and 0.040 and for the protons trans and cis to the radical sites (with respect to a single vinyl group). It is currently not possible to compare this prediction with experimental results since there do not seem to be any examples of esr data taken from two different σ-type radicals prepared from the same parent molecule by removal of nonequivalent hydrogen atoms.

Conclusions

A smooth relationship between the second-order property of a singlet molecule (spin–spin coupling) and a first-order property of a doublet radical (hyperfine splitting) has been demonstrated *via* molecular orbital theory.

Although there is a general lack of experimental data for hyperfine interactions in σ-type neutral radicals, especially for ^{13}C splitting constants, the existing data tend to indicate that the mechanisms responsible for these interactions parallel, to a large extent, the mechanisms responsible for the corresponding nuclear spin coupling constants in the parent molecule. This tentative conclusion is based primarily on the relative constancy of the experimental ratio J_{AB}/α_A for different types of interactions.

The evidence is more convincing from the standpoint of the INDO calculations. The smooth, monotonic, behavior of the curves of s-orbital spin density *vs.* the nuclear spin of a proton, together with the relative constancy of the ratios of initial slope to asymptotic value, indicates that these two phenomena do share substantial fundamental features in common. While this situation does not in itself elucidate the details of the ostensibly common mechanisms, the family of curves provides a foundation for future work into the nature of the mechanisms.

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[14] J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).