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The spin polarization model for hyperfine coupling constants

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Summary. The simple spin polarization model for calculation of the spin densities that determine hyperfine coupling constants in free radicals is examined. Spin-unrestricted approaches, both without and with removal of spin contamination, are discussed and compared with spin-restricted treatments. Basis set design and electron correlation effects are also considered. Calculations on small pi radicals are presented to illustrate the arguments. Explanations are advanced for why some of the simpler treatments seem to work better than might be expected.

Key words: Spin polarization model – Spin density – Hyperfine coupling constants – Pi radicals – Spin contamination – Gaussian basis sets – Electron correlation

1. Introduction

Twenty years ago, when the present author was a graduate student with Professor Hirschfelder at the University of Wisconsin, Joe gave a seminar to the Theoretical Chemistry Institute with the provocative title "Why Simple Models Work". Considering several very different specific examples, Joe pointed out an interesting common feature of simple models: they may often seem to work well in spite of not explicitly treating various physical effects that are known to make substantial contributions. In such situations, there are at least two ways in which a simple model may "work".

One is that the untreated physical effects may often make contributions of about the same magnitude but of opposite signs, thus tending to cancel one another out. If this balance of errors happens under a wide range of conditions, the simple model may appear to be generally valid. However, there will always be some conditions where the cancellation does not occur and the model will appear to break down.

Another is that the physical effects that are not explicitly treated may be correlated with other effects that are. In that case, empirical adjustment of parameters that enter the model may largely account for the influence of the missing effects. This situation is recognized when evaluation of the parameters from first principles gives results quite different from empirical values.

In this issue of *Theoretica Chimica Acta* that commemorates the late Professor Hirschfelder, it seems appropriate to describe how the present author has since encountered both of these situations over and over in various guises. The general field to be considered is theoretical calculation of electronic spin densities that determine the hyperfine coupling constants experimentally observed in free radicals by electron paramagnetic resonance spectroscopy. In particular, the utility of the simple spin polarization model will be examined to attempt to gain insight into why it often seems to "work" so well. This paper constitutes a highly personal view, drawing examples mainly from the present author's own experience in this area of research.

Joe certainly did not mean to criticize the use of simple models. On the contrary, he pointed out that many important advances in science have come from oversimplified ideas. At the same time, he emphasized that any simple model must necessarily have a limited range of applicability. It is important to determine this range and, when situations outside of it are encountered, to learn how to extend the model to treat the relevant "missing" effects. This work is also a contribution to those goals.

First, a general overview is given of various theoretical approaches that are often applied to the spin density problem. Then common Hartree–Fock methods with and without spin restrictions, the latter with and without removal of spin contamination, and single-excitation configuration interaction are discussed and compared in some detail. Next, basis set considerations and then electron correlation effects are examined. Finally, a brief conclusion is provided. Representative literature is cited throughout, but no attempt is made at a comprehensive survey.

2. Overview of methods

The spin density Q at a point $\boldsymbol{r}$ in space may be regarded simply as the density of α-spin electrons minus the density of β-spin electrons at $\boldsymbol{r}$ (where we have arbitrarily assigned the excess spin to be α), normalized to the number of unpaired electrons. Mathematically, this can be defined in terms of the electronic wave function Ψ of the free radical under consideration as:

$$Q(\boldsymbol{r}) = \int \Psi^*(\boldsymbol{x}) \sum_i^{\text{elec}} \delta(\boldsymbol{r}_i - \boldsymbol{r}) 2S_{zi} \Psi(\boldsymbol{x})\, d\boldsymbol{x} \Big/ \int \Psi^*(\boldsymbol{x}) \sum_i^{\text{elec}} 2S_{zi} \Psi(\boldsymbol{x})\, d\boldsymbol{x}$$

where, for simplicity of notation, we suppress the parametric dependence of the wave function on the nuclear coordinates (assuming a clamped-nucleus approximation) and where the integrations range over the space-spin coordinates $\boldsymbol{x}$ of all the electrons. The denominator is simply the number of unpaired electrons in the radical. Note that, despite its name, the spin density is actually a function only of spatial coordinates $\boldsymbol{r}$.

Hyperfine coupling constants (hfcc) of free radicals observed in electron paramagnetic resonance spectroscopy are determined by the electronic spin densities at or near the positions of any magnetic nuclei. The Fermi contact interaction gives rise to an isotropic hfcc for a magnetic nucleus N located at $\boldsymbol{r}_N$ that is directly proportional to the spin density there:

$$a(N) = 8\pi/3 g_e \beta_e g_N \beta_N Q(\boldsymbol{r}_N)$$

Similarly, dipolar interactions give rise to anisotropic hfcc that depend on the spin density in the vicinity of $\mathbf{r}_N$ according to:

$$B_{\mu\nu}(N) = g_e\beta_e g_N\beta_N \int (3r_\mu r_\nu - r_\mu^2\delta_{\mu\nu})r^{-5}Q(\mathbf{r})\,d\mathbf{r}$$

where μ, ν refer to x, y, z and the origin of the coordinate system is taken to be at $\mathbf{r}_N$.

In terms of the different physical effects included in the electronic wave function, mechanisms giving rise to spin density can be broadly classified in a perturbation theory sense as: (a) zero-order direct contributions arising from the orbitals singly occupied by the unpaired electrons; (b) first-order spin polarization contributions indirectly arising from differential exchange interactions of the remaining nominally paired electrons with the unpaired electrons; and (c) second- and higher-order effects arising from electron correlation.

The direct contribution is easily determined from simple Hartree–Fock based models, either with or without spin restrictions. It is often the most important contribution for anisotropic dipolar couplings and, in the case of sigma radicals, for isotropic Fermi contact couplings as well. However, it predicts isotropic Fermi contact couplings to be zero in pi radicals and is not always sufficiently accurate even for sigma radicals, so other spin density mechanisms must also often be examined.

Spin polarization provides important contributions to the hfcc in many radicals. It is the basis underlying commonly used empirical models for pi radicals, such as the McConnell relation [1] for hydrogen hfcc and the Karplus–Fraenkel relation [2] for ^{13}C hfcc. These both take the spin densities at the nuclei to be proportional to the populations of unpaired electrons in the neighboring pi atomic orbitals, which can be easily estimated by, for example, simple Hückel theory calculations. The single determinant spin-unrestricted Hartree–Fock (UHF) wave function, which incorporates in some fashion both direct and spin polarization effects, is the basis for the widely used semiempirical INDO method [3]. The local density functional $X\alpha$ method, which utilizes a spin-unrestricted wave function, has also recently been used for spin density calculations [4].

The UHF wave function is also often used in *ab initio* calculations, sometimes followed by spin annihilation (UHF-AA) [5] or full spin projection (PUHF) [6] to remove spin contamination. The closely related extended Hartree–Fock (EHF) method, which corresponds to orbital optimization *after* spin projection of a spin-unrestricted single determinant wave function, has occasionally been applied [7].

Direct and spin polarization effects are also included in a variety of methods based on a spin-restricted open shell Hartree–Fock (ROHF) wave function augmented by interaction with singly excited configurations (SCI) that couple to it. These include a variant of the semiempirical INDO method [8] as well as *ab initio* approaches carried through first [9] or second order [10] in perturbation theory or treated fully by matrix diagonalization [11]. A closely related symmetry-adapted cluster model [12] (SAC) brings in certain higher order self-consistency effects as well.

Inclusion of true electron correlation effects is much more computationally demanding, generally requiring treatment of many configurations corresponding to double and possibly higher excitations. For this reason, not much is known about the various contributions to hfcc that are lumped together under this heading. Starting from a spin-restricted reference, standard single plus double excitation configuration interaction (SDCI) calculations [13] have often been carried out. Spin-restricted SAC + CI [14] and MBPT(3) [15] calculations have also been reported. A variety of methods to include electron correlation based on spin-unrestricted wave functions have been used to determine spin densities, for example CEPA [16], MBPT(4) [17], CCSD [17], and QCISD [18].

All of these approaches that attempt to recover a substantial portion of the correlation energy are computationally intensive and therefore necessarily limited at present to small systems. For consideration of large, chemically interesting radicals it might be hoped that extensive treatment of electron correlation effects will not always be necessary. Simpler procedures that could reliably determine hfcc within, say, 10–20% of experiment would be very useful for interpretation and analysis of free radical systems.

The partial success of the simpler empirical, semiempirical and *ab initio* procedures that do not include electron correlation suggests that spin polarization effects alone may provide a satisfactory account of the hfcc in many radicals. However, there are numerous systems where such methods have seemed to fail in giving a good representation of the hfcc. In spin-unrestricted approaches, a complicating feature is that it is not theoretically apparent in general whether or not spin contamination effects should be removed. In practice such removal often improves results, but sometimes it makes them worse. Another unfortunate circumstance is that many of the previous *ab initio* calculations aiming to include spin polarization effects have used basis sets that are now known to be inadequate for proper description of hfcc. Recently, a [631|41] basis has been developed for reliable spin polarization calculations [19]. We use this here in conjunction with spin-restricted wave functions to unambiguously investigate the range of validity of the spin polarization model.

The MELDF [20] program was used for the configuration interaction calculations reported here. UHF and PUHF calculations utilized a modified version of GAUSSIAN 76 [21], and MCSCF calculations were performed with the COLUMBUS [22] program system.

In free atoms and diatomics, the high spatial symmetry allows spin and orbital polarization effects to be separated and considered independently. However, in most polyatomic molecules they are difficult to separate and consequently are generally treated together. It should therefore be pointed out that the term "spin polarization model" is usually loosely taken to include direct, spin polarization and orbital polarization effects all together, and the term will be used in that sense in this work.

2.1. ROHF method

The simplest spin-restricted high-spin open shell wave function for $2m+n$ electrons corresponds to a single configuration constructed as an antisymmetrized product of one-electron functions. Paired electrons are placed two at a time (with opposite spins) into the m lowest energy doubly occupied orbitals (DOMOs) and the unpaired electrons are placed in n higher energy singly occupied molecular orbitals (SOMOs) with parallel spins. The wave function is then simply the single Slater determinant:

$$\Psi^{\mathrm{ROHF}} = A[\psi_1(1)\bar{\psi}_1(2)\cdots\psi_m(2m-1)\bar{\psi}_m(2m)\psi_{m+1}(2m+1)\cdots\psi_{m+n}(2m+n)]$$

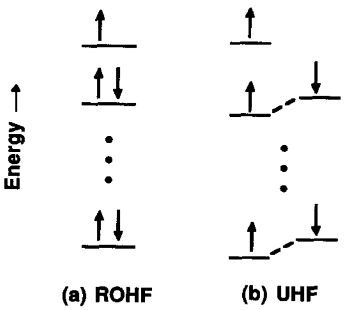

Fig. 1. Schematic diagram of energy levels and electron occupations for orbitals in a doublet free radical

In the following, it is important to keep in mind the distinction between a molecular orbital (MO), which is a function only of the spatial coordinates of an electron, and a spin-orbital, which corresponds to a MO multiplied by an appropriate spin function α or β. Note that the wave function here is spin-restricted, i.e., the two spin-orbitals in a pair are constrained to have identical MOs. If the MOs are determined by a self-consistent-field (SCF) optimization procedure, this is referred to as the spin-restricted open shell Hartree–Fock (ROHF) wave function.

The one-electron energy levels in this model are thus occupied as in Fig. 1a for the special case of a doublet radical. The DOMOs $\psi_1 \cdots \psi_m$ make no net contribution to the spin density because the contribution from any α-spin electron is exactly cancelled by an identical contribution of the opposite sign from its partner β-spin electron. The spin density in this model is then just due to the sum of the probability distributions of the SOMOs:

$$Q^{\mathrm{ROHF}}(\boldsymbol{r}) = \sum_{j=1}^{n} |\psi_{m+j}(\boldsymbol{r})|^2$$

This characterizes the direct contribution to the total spin density, which is clearly always nonnegative.

Consider the planar methyl radical as a simple example. The results in Table 1 show that the ROHF method gives a reasonable account of the anisotropic hfcc, but gives exactly zero for the isotropic hfcc. This latter shortcoming is due to the fact that the SOMO is a p orbital perpendicular to the molecular plane. It therefore has a node at all the nuclei and so cannot contribute to the contact spin density.

The direct contribution, which is the easiest to calculate, can often be the dominant one for anisotropic hfcc and, in some sigma radicals, may also dominate the isotropic hfcc. But it has some serious shortcomings for isotropic hfcc in general. This is particularly noticeable in pi radicals, as we have just seen, and may also be important in some sigma radicals. Clearly, there must be some other important mechanism or mechanisms at work in such systems.

2.2. UHF method

The most important of the other mechanisms is the indirect spin polarization contribution. Although not necessarily the best means to calculate it in practice, the source of spin polarization is most easily described in connection with a spin-unrestricted single-configuration wave function. The effect is ultimately due

Table 1. Hyperfine coupling constants in Gauss for planar methyl radical[a] calculated from various wave functions

Method	$a(^{13}C)$	$a(^{1}H)$	$B_{xx}(^{13}C)$	$B_{xx}(^{1}H)$	$B_{zz}(^{1}H)$
UHF/[631|41]	57.8	−41.7	52.7	−0.6	16.4
PUHF/[631|41]	20.2	−13.6	53.8	0.1	13.5
ROHF/[631|41]	0.0	0.0	53.5	0.7	11.8
SCI/[631|41]	26.6	−25.6	53.0	−0.2	14.7
Experiment[b]	27[c]	−25[c]	45[d], 43.4[e]	0.5[d], 0.8[e], 0.5[f,g]	12.5[g]

[a] D_{3h} symmetry and the experimental [23] CH bond length of 1.079 Å are assumed. The x direction is perpendicular to the molecular plane and z is parallel to the bond joining carbon with the hydrogen listed here

[b] The "experimental" isotropic hfcc listed here have been corrected [11] to remove the effects of out-of-plane bending. Uncorrected experimental values are listed for the anisotropic hfc[c], since the corrections there are small [11]

[c] Ref. [11]

[d] Ref. [24]

[e] Ref. [25]

[f] Ref. [26]

[g] Ref. [27]

to the Pauli exclusion principle, which gives rise to nonclassical exchange interactions among the electrons. The key point is that this exchange interaction only operates between electrons of the same spin.

Consider a pair of electrons described by DOMO $\psi_k\bar{\psi}_k$ in a spin-restricted single configuration wave function such as discussed in the previous section. They will experience identical coulomb interactions with the nuclei and with the other electrons, and identical exchange interactions with all the other pairs of electrons in DOMOs. But the α-spin electron in this pair will experience an additional exchange interaction with each of the unpaired electrons (in the SOMOs) that is not sensed by its β-spin partner. If the two spin-orbitals in the pair are allowed to relax separately, they will then differentially polarize into slightly different optimum MOs, i.e., the relaxed pair will be described as $\psi_k^\alpha\bar{\psi}_k^\beta$. The wave function then can be written as the single Slater determinant:

$$\psi^{\mathrm{UHF}} = A[\psi_1^\alpha\bar{\psi}_1^\beta \cdots \psi_k^\alpha\bar{\psi}_k^\beta \cdots \psi_m^\alpha\bar{\psi}_m^\beta\psi_{m+1}^\alpha \cdots \psi_{m+n}^\alpha]$$

If the MOs are determined by an SCF optimization procedure, this is referred to as the spin-unrestricted Hartree–Fock (UHF) wave function. The one-electron energy levels in this model are occupied as in Fig. 1b, which is meant to schematically show the splitting of each nominally doubly occupied pair. The two MOs ψ_k^α and ψ_k^β of a particular pair are likely very similar to one another, but will not be exactly the same. They no longer then exactly cancel one another in the total spin density, which is given in this model by:

$$Q^{\mathrm{UHF}}(\boldsymbol{r}) = \sum_{j=1}^{n} |\psi_{m+j}^\alpha(\boldsymbol{r})|^2 + \sum_{k=1}^{m} (|\psi_k^\alpha(\boldsymbol{r})|^2 - |\psi_k^\beta(\boldsymbol{r})|^2)$$

The first sum is easily recognized as the direct contribution from the unpaired electrons and, aside from minor differences in the optimized orbitals found in each model, is essentially the same as that obtained from the ROHF method. The second sum is the spin polarization contribution from the remaining "paired" electrons. Note that if $\sum_k |\psi_k^\beta(\boldsymbol{r})|^2$ happens to be larger than $\sum_k |\psi_k^\alpha(\boldsymbol{r})|^2$ at some position $\boldsymbol{r}$, the net spin polarization contribution to the spin density there will be negative.

This model provides an appealing physical explanation of the common occurrence of negative spin densities. As a simple illustrative example, consider again the planar methyl radical. We have already seen that there is no direct contribution from the π unpaired electron itself. The remaining "paired" electrons are in sigma orbitals. The valence sigma orbital pairs contribute to the bond connecting carbon to each hydrogen. As noted above, the α-spin member of each such pair experiences an additional exchange interaction with unpaired electron on carbon that is not experienced by its partner β-spin electron. At large distances the exchange interaction is weakly attractive, so an α-spin electron in the vicinity of a hydrogen atom is pulled toward the carbon, thereby slightly depleting the density of α-spin electrons at the hydrogen nucleus. This leaves behind a slight excess of β-spin electrons at the hydrogen, i.e. a negative spin density there. A similar explanation leads one to expect that the $1s$ core pair localized on carbon will make a negative contribution to the spin density at the carbon nucleus.

Table 1 includes UHF results for planar methyl radical. Compared to experiment, it is seen that the anisotropic hfcc are given reasonably well but the isotropic hfcc are much too large in magnitude. This is the usual situation with pi radicals. However, there are some instances where UHF gives results that are about right or even too low. The only general conclusion that can be reached is that UHF may give good isotropic hfcc for some sigma radicals that are dominated by the direct contributions, but it is often quantitatively unreliable when spin polarization effects are important.

One might well wonder how the semiempirical INDO method, which is based on a UHF wave function, can "work" so well in many instances. For example, with planar methyl radical it gives [3] $a(^{13}\text{C}) = 45.0$ G and $a(^{1}\text{H}) = -22.4$ G. This corresponds to very good agreement with experiment for $a(^{1}\text{H})$ and substantial error for $a(^{13}\text{C})$, which however is still considerably closer to experiment than the *ab initio* UHF result (see Table 1).

In the INDO procedure, the UHF wave function is actually used only to determine the spin population in the appropriate s orbital on the atom of interest, e.g. $1s$ on hydrogen and $2s$ on first-row atoms. The Fermi contact spin density is then evaluated separately by multiplying this spin population by a parameter representing the square of the amplitude of this orbital at the nucleus. But this parameter is not determined from the wave function itself. In fact, the $2s$ orbital in each first-row atom is actually represented in INDO by a nodeless Slater-type orbital having zero amplitude at the nucleus. Instead, it is parametrized by least squares fitting to obtain the best overall agreement of the calculated hfcc with experimental values. It is quite impressive that so many good results can be obtained from a method having just one disposable parameter for each element.

Compared to the true hydrogen atom wave function, the INDO parameter representing $|1s_H|^2$ is only 6% too high. Since *ab initio* UHF results are generally a factor of two or more too high for hydrogen hfcc, this indicates that the INDO wave function, in order to produce reasonable hfcc, must provide much smaller hydrogen atom spin populations. Furthermore, this must be a very systematic discrepancy between the *ab initio* UHF and semiempirical INDO wave functions.

It is known [2, 11, 13] that the carbon 1*s* core contribution in methyl is large and negative, acting to partially cancel a very large positive valence contribution to $a(^{13}C)$. The reasonable results obtained by INDO for ^{13}C hfcc, which are usually [3] closer to experiment than seen here for methyl, is therefore interesting since INDO does not even treat the core electrons explicitly. It has been shown [11], however, that the contribution from the 1*s* core electrons is proportional to that of the 2*s* electrons over a wide range of conditions in methyl, so that their influence can be effectively brought in by the empirical adjustment of $|2s_C|^2$. The parametrized value of $|2s_C|^2$ is therefore well below [28] the value obtained from accurate SCF calculations. The proportionality breaks down, however, for significant stretches in bond lengths [11] so INDO may not work well for radicals in unusual bonding situations or far from their equilibrium geometries, such as might be encountered in examining some vibrational corrections.

2.2.1. Spin contamination in UHF. One general criticism of the UHF method is that the wave function does not correspond to a pure spin state. For example, a nominal doublet UHF wave function actually contains contamination from quartet, sextet, and higher spin states. There is a long standing controversy over whether or not it is advisable to remove this spin contamination before evaluation of spin properties. A strong argument against removal comes from a formal analysis [29] showing that UHF gives the correct diagrams in a perturbation theory development of the exact wave function, whereas ad hoc removal of spin contamination does not. But in practice, UHF is often found to give hfcc much larger than experiment, while removal of spin contamination leads to somewhat better agreement. In this section we offer an opinion on the controversy. But first, a brief discussion on the nature of the spin contamination is in order.

The source of spin contamination can be clearly seen through a perturbation theory approach to the UHF wave function in which the ROHF wave function serves as the zero-order approximation. Detailed derivations can be found in several places [29–33] so we give here only an outline of the results. For simplicity, only the doublet case will be explicitly considered. Generalization to an arbitrary high-spin open shell is straightforward and brings in no essential new features.

The doublet UHF wave function for $2m + 1$ electrons can be written:

$$\Psi^{\mathrm{UHF}} = A[\psi_1^\alpha \bar{\psi}_1^\beta \cdots \psi_k^\alpha \bar{\psi}_k^\beta \cdots \psi_m^\alpha \bar{\psi}_m^\beta \psi_{m+1}^\alpha]$$

All of the orbitals ψ_k^α can freely be taken as mutually orthonormal, as can the orbitals ψ_k^β, since any nonorthogonalities within each set would be removed by antisymmetrization anyway. Most UHF computer programs produce "canonical" orbitals for which each member of one set may overlap all members (of the same spatial symmetry) in the other set. However, the invariance of ψ^{UHF} to unitary transformations within each set makes it possible to find "corresponding" orbitals [34] such that each orbital in one set is orthogonal to all orbitals in the other set except for one (if any) with which it is paired. Thus:

$$\langle \psi_k^\alpha | \psi_l^\beta \rangle = S_k \delta_{k,l}$$

This greatly simplifies the analysis, and we assume it has been arranged. It is also assumed that the phases of the orbitals are adjusted to make the overlap integrals S_k all real and positive.

The natural orbitals of the UHF wave function [34] consist of ψ^{α}_{m+1} for the open shell electron and, for the paired electrons, the orthonormal sums and differences of the corresponding orbitals, viz:

$$\psi_k = (\psi^{\alpha}_k + \psi^{\beta}_k)/2\mu_k \qquad \mu_k = \sqrt{(1+S_k)/2}$$

$$\psi^{*}_k = (\psi^{\alpha}_k - \psi^{\beta}_k)/2\lambda_k \qquad \lambda_k = \sqrt{(1-S_k)/2}$$

With these, the two orbitals describing the kth UHF pair can be expressed as:

$$\psi^{\alpha}_k = \mu_k\psi_k + \lambda_k\psi^{*}_k$$
$$\psi^{\beta}_k = \mu_k\psi_k - \lambda_k\psi^{*}_k$$

One can expect that the corresponding orbitals ψ^{α}_k and ψ^{β}_k will be very similar to one another so that the average natural orbital ψ_k will be essentially the same as the ROHF orbital describing this pair. The difference natural orbital ψ^{*}_k provides spin polarization for this pair. One also expects that the overlap integral S_k will be near unity so that μ_k is also near unity and λ_k is a small number.

We now expand the UHF wave function in powers of the small numbers λ_k. Terms will be kept only through first order. Since μ_k differs from unity only by terms of second and higher order in λ_k, it can be replaced by unity for the present purposes. The UHF wave function then becomes:

$$\Psi^{\mathrm{UHF}} = \Psi^{\mathrm{ROHF}} + \sqrt{2}\sum_{k=0}^{m} \lambda_k \Psi_k + \cdots$$

The zero-order term that is independent of all the λ_k is essentially the ROHF wave function:

$$\Psi^{\mathrm{ROHF}} = A[\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}]$$

By itself, this term provides a direct contribution to the spin density from ψ_{m+1}, but no spin polarization contribution because the paired orbitals are exactly doubly occupied. The first-order correction terms linear in the λ_k have wave functions corresponding to $\psi_k \rightarrow \psi^{*}_k$ single excitations from Ψ^{ROHF}, viz:

$$\begin{aligned}\Psi_k = \sqrt{1/2}(&A[\psi_1\bar{\psi}_1 \cdots \psi^{*}_k\bar{\psi}_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &+ A[\psi_1\bar{\psi}_1 \cdots \bar{\psi}^{*}_k\psi_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}])\end{aligned}$$

Double excitations from Ψ^{ROHF} would contribute to terms quadratic in the $\lambda_k\lambda_1$, etc.

The normalized singly excited terms Ψ_k are not eigenfunctions of the total spin operator S^2. They can be expressed in terms of linear combinations of spin eigenfunctions as:

$$\Psi_k = \sqrt{1/3}\Psi^{D}_k + \sqrt{2/3}\Psi^{Q}_k$$

where

$$\begin{aligned}\Psi^{D}_k = \sqrt{1/6}(&A[\psi_1\bar{\psi}_1 \cdots \psi^{*}_k\bar{\psi}_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &+ A[\psi_1\bar{\psi}_1 \cdots \bar{\psi}^{*}_k\psi_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &- 2A[\psi_1\bar{\psi}_1 \cdots \psi^{*}_k\psi_k \cdots \psi_m\psi_m\bar{\psi}_{m+1}]) \\ \Psi^{Q}_k = \sqrt{1/3}(&A[\psi_1\bar{\psi}_1 \cdots \psi^{*}_k\bar{\psi}_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &+ A[\psi_1\bar{\psi}_1 \cdots \bar{\psi}^{*}_k\psi_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &+ A[\psi_1\bar{\psi}_1 \cdots \psi^{*}_k\psi_k \cdots \psi_m\psi_m\bar{\psi}_{m+1}])\end{aligned}$$

Here Ψ_k^D is a pure doublet while Ψ_k^Q is a quartet and is the main source of spin contamination. It is important to note that this resolution into spin eigenfunctions has forced the introduction of a new term involving a spin-flip of the open shell electron, i.e., $\psi_{m+1} \rightarrow \bar{\psi}_{m+1}$.

Second and higher order correction terms bring in still other spin contaminants. For a nominal doublet, these correspond to sextet, octet, etc., spin states. In practice, the magnitudes of these higher order terms vary from system to system, sometimes being quite important and other times being negligible.

Brillouin's theorem guarantees that any configuration differing from $\Psi^{\rm ROHF}$ by only one spin orbital will not connect with it in the Hamiltonian matrix. In effect, the variational SCF procedure for orbital optimization folds such terms into $\Psi^{\rm ROHF}$ itself, making it stable to first order against such excitations. This applies to all single excitations of the open shell electron such as $\psi_{m+1} \rightarrow \psi^*_{m+1}$. It applies to a $\psi_k \rightarrow \psi_k^*$ excitation of a paired electron only for the spin coupling that corresponds in a genealogical construction to first making a singlet coupling of ψ_k with ψ_k^* and then finally coupling ψ_{m+1} to produce the resultant doublet. Due to Brillouin's theorem, these kinds of configurations do not appear in the above development.

The spin eigenfunction for Ψ_k^D corresponds instead to first making a triplet coupling of ψ_k with ψ_k^*, and then finally coupling ψ_{m+1} to produce the resultant doublet. This configuration connects with $\Psi^{\rm ROHF}$ in both the Hamiltonian and the spin density matrix. This is because one of the terms contains $\bar{\psi}_{m+1}$, i.e., a spin-flip of the open shell electron, and therefore differs from $\Psi^{\rm ROHF}$ in two spin-orbitals. The historical preoccupation of quantum chemistry with closed shell systems has left a semantic ambiguity about the precise meaning of "excitation level" in open shell systems. Here we see that a single spatial excitation can lead to a change of two spin-orbitals in the wave function, so Ψ_k^D could reasonably be called either a single or a double excitation depending on whether one is referring to differences in MOs or in spin-orbitals. We prefer a nomenclature in which a term such as this is described as a "single excitation". Since the variational principle is sensitive to differences in spin-orbitals, this requires keeping in mind that Brillouin's theorem does not apply to all "single excitations" in open shell systems.

Putting together the above relations, the UHF wave function through first order can now be written as:

$$\Psi^{\rm UHF} \eqsim \Psi^{\rm ROHF} + \sqrt{2/3} \sum_{k=0}^{m} \lambda_k (\Psi_k^D + \sqrt{2}\Psi_k^Q)$$

A calculation allowing full variational freedom to the coefficients of Ψ_k^D and Ψ_k^Q would lead to zero weight for Ψ_k^Q since it is of the wrong total spin. However, we see here that the UHF method does not allow full variational freedom to these two coefficients, but instead fixes their relative proportions at the outset and optimizes only one particular linear combination of them. Therefore, Ψ_k^D will have a nonoptimal weight in the UHF wave function due to the enforced presence of the spin contaminants.

The PUHF wave function through first order corresponds to simply eliminating the spin contaminant to obtain:

$$\Psi^{\rm PUHF} \eqsim \Psi^{\rm ROHF} + \sqrt{2/3} \sum_{k=0}^{m} \lambda_k \Psi_k^D$$

UHF-AA is the same as PUHF in this low order treatment, although they differ in the higher orders. While the projected wave function is a pure doublet, it can still be criticized in that the coefficients of the first-order correction terms in Ψ_k^D, having been carried over unchanged from the UHF wave function, are still not determined from an unconstrained variational optimization.

The spin density through first order is given in each method by:

$$Q^{\mathrm{ROHF}}(r) = |\psi_{m+1}(r)|^2$$

$$Q^{\mathrm{UHF}}(r) = |\psi_{m+1}(r)|^2 + 4 \sum_{k=0}^{m} \lambda_k \psi_k(r) \psi_k^*(r) + \cdots$$

$$Q^{\mathrm{PUHF}}(r) = |\psi_{m+1}(r)|^2 + 4/3 \sum_{k=0}^{m} \lambda_k \psi_k(r) \psi_k^*(r) + \cdots$$

Each of these procedures has the same zero-order direct contribution. The latter two have first-order spin polarization corrections of the same general form, but with different values of the coefficients. The coefficient of $4\,\lambda_k$ multiplying each UHF spin polarization correction term can be traced to contributions of $4/3\,\lambda_k$ coming from Ψ_k^D and $8/3\,\lambda_k$ coming from Ψ_k^Q, the latter being allowed because functions of different total spin can connect in matrix elements over the spin density operator. Upon projection, only the $4/3\,\lambda_k$ contribution from Ψ_k^D remains so that the net PUHF spin polarization correction is only one-third as large as in UHF. This factor of 1/3 becomes $n/(n+2)$ in the more general case of a high-spin open shell holding n electrons, e.g., 1/2 for a triplet, 3/5 for a quartet, etc. In cases of significant spin contamination from higher states, the first-order analysis is less accurate and these simple relations break down.

Having seen how it arises, we are now in a position to address the question of whether or not such ad hoc removal of spin contamination is advisable. The real question is which of the coefficients $4\,\lambda_k$ or $4\lambda_k/3$ produced by the unprojected or projected procedures, respectively, is closest to that which would be obtained from a variationally unconstrained CI calculation over the configurations Ψ^{ROHF} and the Ψ_k^D. Using an uncoupled approximation to perturbation theory, Nakatsuji [32] has obtained explicit expressions for these coefficients, thereby providing a means to answer this question. He finds in lowest order that the λ_k of the UHF and PUHF procedures are given by:

$$\lambda_k = \frac{\frac{1}{2}\langle \psi_k^* | \hat{K}_{m+1} | \psi_k \rangle}{(\langle \Psi_k^D | \hat{H} | \Psi_k^D \rangle - E^{\mathrm{ROHF}}) - (K_{m+1,k} + K_{m+1,k^*} + K_{k,k^*})}$$

Note that the denominator consists of the difference between a promotion energy, which is positive, and a sum of three exchange integrals, which are also positive. (The EHF method provides coefficients similar to this, but with the sum of the three different exchange integrals replaced by $3\,K_{k,k^*}$, and is subject to arguments similar to those given below in connection with UHF.) Nakatsuji [32] further finds that the optimum coefficient from an unconstrained variational CI calculation is also similar to this, but missing all the exchange integrals in the denominator. If these exchange integrals happen to be small compared to the promotion energy, then the coefficients provided by the UHF method will be near the optimal ones and the UHF spin density will be accurate. On the other hand, larger values of the exchange integrals will lead to a smaller denominator and so make the UHF spin polarization too large. In the latter situation, a procedure that reduces the spin polarization contribution may give better results.

However, there is no theoretical justification for reducing it by the particular factor of 1/3 that is found in PUHF.

In fact, the situation may vary for different electron pairs in the same radical. This has apparently actually been observed in the case of the carbon hfcc in planar methyl radical [11]. It was found there that the UHF method gives the carbon 1*s* core contribution about right, and that the large net overestimation of the hfcc comes from a valence contribution that is much too large. The PUHF result gives better apparent agreement with experiment, but by indiscriminately multiplying all the contributions by about 1/3 it obtains a separate 1*s* core contribution that is much smaller than the correct one.

The theoretical considerations can therefore be deemed inconclusive on the question raised at the beginning of this section. Some support may be given to UHF, but only under particular conditions that may not often be met in practice. UHF will generally give spin polarization contributions that are too large. Spin projection acts to reduce the spin polarization contribution, and so may appear to give better results in certain instances, but there is no real theoretical justification for it.

Rather than consider theoretical arguments, the issue is more often judged by results of actual applications. We give PUHF results for planar methyl radical in Table 1. The anisotropic hfcc, which are dominated by the direct contribution, are indeed little changed by spin projection and the isotropic hfcc, which arise only from the spin polarization contribution, are indeed reduced by about a factor of three, as predicted. Compared to experiment, the UHF results are much too high and the PUHF results are somewhat too low for the isotropic hfcc in Table 1, the PUHF results being closer to experiment. Results such as this are typical for hydrocarbon pi radicals [35, 36]. Such findings by many workers have led to a general perception that annihilation and/or projection is desirable in general for computing spin properties from a UHF wave function.

Contrary examples come from recent studies on the H_2CN [37] and ethyl [38] radicals. The large β-hydrogen hfcc in these systems are due to approximately equal contributions from direct, spin polarization, and electron correlation effects. In both cases UHF gives a good result, while PUHF is much too small. Actually, the apparently good UHF result is fortuitous, a consequence of its overestimation of the spin polarization contribution accidentally being about the right magnitude to make up for the electron correlation contribution that it ignores. Interestingly, the other hfcc in these radicals follow the more common situation of UHF being much too large and PUHF a little too small.

In summary, neither UHF nor PUHF can be given firm theoretical support for calculation of spin densities. Computational results, when carefully analyzed, are indecisive as well. The "improvement" in UHF spin properties often seen after annihilation and/or full projection is accidental and can not be counted on in general. Since such methods can not be trusted to provide uniformly accurate results, this author has more recently turned instead to spin-restricted approaches for this problem.

3. Single excitation configuration interaction

As intimated in the previous section, spin polarization can be less ambiguously introduced via a fully spin-restricted framework. Beginning with the occupied MOs $\{\psi_k\colon k = 1 \ldots m+1\}$ used to build up the doublet ROHF wave function, let $\{\chi_t\}$ be a set of orthonormal virtual MOs that span the remainder of the space within the given basis set. Then augmenting the ROHF wave function with all spin polarization single excitations leads to what might be called the SP-SCI method, viz:

$$\Psi^{\text{SP-SCI}} = c_0 \Psi^{\text{ROHF}} + \sum_{k=1}^{m} \sum_{t} c_{k,t} \Psi^{D}_{k,t}$$

where

$$\begin{aligned}\Psi^{D}_{k,t} = \sqrt{1/6}(&A[\psi_1\bar{\psi}_1 \cdots \chi_t\bar{\psi}_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &+ A[\psi_1\bar{\psi}_1 \cdots \bar{\chi}_t\psi_k \cdots \psi_m\bar{\psi}_m\psi_{m+1}] \\ &- 2A[\psi_1\bar{\psi}_1 \cdots \chi_t\psi_k \cdots \psi_m\psi_m\bar{\psi}_{m+1}])\end{aligned}$$

The $\Psi^{D}_{k,t}$ are configurations with triplet intermediate coupling of ψ_k and χ_t, just as discussed in the previous section. Recall that such configurations couple with Ψ^{ROHF} both in the Hamiltonian matrix and in the spin density matrix.

The analogy with the unconstrained variational calculation discussed in the previous section can be made closer by collapsing the sum over virtual orbitals into a single normalized spin polarization orbital characteristic of each pair:

$$c_k \psi^*_k = \sum_t c_{k,t} \chi_t$$

With this we have the compact description

$$\Psi^{\text{SP-SCI}} = c_0 \Psi^{\text{ROHF}} + \sum_{k=1}^{m} c_k \Psi^{D}_{k}$$

with Ψ^{D}_{k} having precisely the same form as in the previous section. A little more manipulation is required to give this SP-SCI wave function the same properties as in the previous section, because the ψ^*_k orbitals obtained here may not be mutually orthogonal. A linear transformation can be carried out among the ψ^*_k to bring about their orthonormality. This alone would generate extra configurations corresponding to interpair excitations, but a simultaneous unitary transformation can be carried out among the ψ_k to preserve a wave function of the above form having just one spin polarization configuration for each pair of electrons. These considerations uniquely determine the orbital mixings, except possibly for mixing within small degenerate sets in cases of high spatial symmetry, and provide orbitals very similar to those discussed previously in connection with the UHF and PUHF procedures. In fact, the ψ_k and ψ^*_k so obtained are the SP-SCI charge density natural orbitals for pair k. Furthermore, the SP-SCI spin density natural orbitals for pair k are simply their normalized sums and differences [11]. Because there are no terms coupling different pairs, these allow for a useful decomposition of the spin density into separate contributions from each individual pair of electrons.

A full single excitation (SCI) calculation should also give similar results since Brillouin's theorem implies that the additional single excitations included would make only small contributions. Another possibility is to determine the orbitals in both the reference determinant and the spin polarization configurations self-consistently by what might be called a SP-MCSCF calculation [39, 40]. The SAC method [12] is a variation on that theme in which still higher order self-consistency effects are brought in. The UHF and PUHF models share the same natural orbitals, differing only in their occupation numbers [6], and these are also very similar to the natural orbitals of the SP-SCI method [11]. This suggests that

Table 2. Hyperfine coupling constants in Gauss for methyl, ethyl, and allyl radicals

Method	$a(^{13}C_\alpha)$	$a(^{13}C_\beta)$	$a(^{1}H_\alpha)$	$a(^{1}H_\beta)$
	CH_3 (ν_2 vibrational average[a])			
SCI/[631|41]	36.2		−23.9	
Experiment	38.3[b]		−23.0[b]	
	C_2H_5 (ν_6 vibrational average[c])			
SCI/[631|41]	39.7	−14.0	−24.0	19.4
Experiment	39.1[b]	−13.6[b]	−22.4[d]	26.9[d]
		C_3H_5[e]		
SCI/[631|41]	18.0	−19.6	−14.1, −15.1	2.1
Experimental	21.9[f]	−17.2[f]	−13.9[f], −14.8[f]	4.2[f]

[a] The geometry used for the methyl radical calculation is given in footnote (a) of Table 1. The procedure used to carry out the vibrational average over the ν_2 large amplitude out-of-plane bend at carbon is described in Ref. [11]

[b] Ref. [42]

[c] The ethyl radical calculations are taken from Ref. [38]. The geometry is based on the MCSCF/6-31G** calculation of Ref. [43]. The procedure used to carry out the vibrational average over the ν_6 large amplitude out-of-plane bend at the α-carbon is described in Ref. [38]. The three calculated β-hydrogen hfcc for the almost freely rotating methyl group have been averaged for comparison to experiment

[d] Ref. [44]

[e] The allyl radical calculations are carried out at the geometry determined in the ACPF/MIDI3* calculation of Ref. [45]

[f] Ref. [46]

UHF-based procedures determine the spin polarization orbitals themselves well, although not the weights of the configurations in which they appear. Another compact description of the spin polarization effects can therefore be obtained by carrying out a small CI calculation over spin-restricted configurations constructed from the UHF natural orbitals [31, 41]. In practice, it probably doesn't make too much difference which of these methods is employed, or any of many other variations that can be imagined. All are physically based on describing the lowest order spin polarization effects in a spin-restricted framework and should give similar results in most applications.

Results on planar methyl radical from the SCI method are given in Table 1. It is seen that the method gives very close agreement with experiment for the isotropic hfcc and results of about the same quality as the other methods considered for the anisotropic hfcc. We therefore confirm that the simple spin polarization model is quite good for methyl, and that the problem with UHF and PUHF methods must be in the artificial constraints they place on the weights of the spin polarization terms.

SCI/[631|41] results for the isotropic hfcc of methyl, ethyl and allyl radicals, including vibrational corrections for the large amplitude out-of-plane bending at C_α in methyl and ethyl, are collected in Table 2. The results for methyl are very close to experiment, as are those of ethyl with the single exception that $a(H_\beta)$ is 28% too low. Comparing the allyl results to experiment, $a(C_\alpha)$ is 18% too low, the magnitude of $a(C_\beta)$ is 14% too high, and both the $a(H_\alpha)$ are good. The value of $a(H_\beta)$ in allyl is lower than experiment, the modest 2.1 G absolute error appearing as a large 50% relative error because of the small magnitude of the coupling constant.

We see here that the spin polarization model (as exemplified by the SCI/[631|41] results) applied to the methyl, ethyl, and allyl radicals gives good isotropic hyperfine coupling constants for carbons and for α-hydrogens, but gives low values for β-hydrogens. In SCI/[631|41] calculations on the nitrogen centered H_2CN radical [37], we have found similar good results at nitrogen and carbon, but a 33% underestimate of the large values at the β-hydrogens. It is tentatively concluded that the spin polarization model generally does well for first-row atoms and α-hydrogens, giving results well within 20% of experiment, but systematically underestimates β-hydrogen hfcc.

4. Basis sets

It is unfortunate that many of the early studies on hfcc were flawed by the use of basis sets that are now known to be inadequate for the purpose. In this section we discuss some important considerations in design of basis sets for use in spin density calculations.

The use of Gaussian functions for determination of Fermi contact spin densities has sometimes been criticized because any finite set of Gaussians is inherently unable to satisfy the correct cusp condition associated with the singularity of the potential at the nucleus. This is essentially a constraint on the derivative of the wave function [47] and cannot be met because *s*-type Gaussians arrive at the nucleus with zero radial slope. Of course, in a molecule there may be some contribution to the cusp at one nucleus from the tails of Gaussians centered at other nuclei, but such contributions are generally much too small to allow for satisfaction of the cusp condition.

We believe, however, that this criticism is unwarranted and that the difficulty in satisfying the correct cusp condition is not really that important for spin density calculations with Gaussian basis sets. The Fermi contact interaction depends on the amplitude of the *s* orbital at the nucleus, not on its derivative. By proper design of a Gaussian basis set, it is possible to approach arbitrarily closely to the correct amplitude at the nucleus. There is a problem, however, in that most common Gaussian basis sets were designed mainly to describe the chemically important valence regions, and have not been prepared to describe the regions near the nuclei well.

Based on the fact that Slater-type orbitals have more proper behavior near the nucleus, two indirect approaches have been suggested for correcting this problem in Gaussian basis calculations. One [48] applies a correction factor determined by comparison to calculations on the charge density at the nucleus of the free atom, which has independently been accurately determined using Slater-type orbitals. Another [49] utilizes STO-6G Gaussian basis sets to first determine the electronic wave function, then replaces these with the corresponding true Slater-type orbitals for the subsequent hfcc evaluation step, assuming no change in the expansion coefficients.

We have chosen [19] instead a more direct procedure to resolve this problem by simply including additional tight (i.e., short range, large exponent) *s* functions in the basis. It has been found that such tight *s* functions can be contracted in with the existing innermost functions, using contraction coefficients determined by simple ROHF calculations. With the popular Huzinaga [50] $(9s5p|4s)$

primitive basis, it was found that the improper behavior of the *s*-type Gaussian functions near the origin leads to an underestimate of about 5% in the spin density at first-row atom nuclei, and a larger 15% error for hydrogen. The 5% error at the first-row atoms may often be acceptable in spin polarization calculations, where effects due to electron correlation, geometry uncertainties, and vibrational corrections may lead to other errors of this or larger magnitude anyway. However, the 15% error at hydrogen is unacceptably large and we recommend routinely including a tight *s* function at hydrogen, which brings the error there down to about 6–7%. If higher accuracy is sought, one can add a tight *s* function to each first-row atom and a second tighter *s* function to hydrogen to bring this error down to the 2–3% range [19]. Adding yet another tighter *s* function at each atom would bring these errors down to less than about 1%.

These considerations can be different for other basis sets. For example, the large energy optimized van Duijneveldt Gaussian basis sets [51] already have very high exponent *s* functions and can be utilized as they stand in most spin density calculations. Even-tempered Gaussian sequences [52], on the other hand, are quite weak in this respect and would require very long expansion lengths to provide adequate amplitude at the nucleus. Some means of correcting this behavior, such as discussed above, is necessary if even-tempered Gaussian sequences of reasonable expansion length are to be used for accurate spin density calculations.

The [631|41] contracted Gaussian basis we have been using in this work, which corresponds to the $[5s2p1d|3^{\dagger}s1p]$ + diffuse *sps* basis in the notation of our earlier study [19], was developed especially for spin polarization calculations of hfcc by comparing to accurate numerical SP-MCSCF calculations on the free first-row atoms and their diatomic hydrides. It is based on a $(10s6p1d|6s1p)$ primitive cartesian Gaussian basis that includes the $(9s5p|4s)$ standard Huzinaga primitive basis augmented with diffuse functions [53] (*sp* on first-row atoms, *s* on hydrogen), a tight (high exponent) *s* function on hydrogen, and polarization functions (*d* on first-row atoms, *p* on hydrogen). Only the innermost few primitives are contracted, i.e., the contraction groupings are (511111,411,1|3111,1).

Spin polarization calculations with this basis set are compared to those of other common basis sets in Table 3 for several small hydrocarbon pi radicals. The [631|41] results give good agreement with experiment, indicating that the spin polarization model itself is adequate for these cases. However, it is seen that smaller basis sets sometimes give erratic results.

The split valence 6-31G basis set [56] and the related 6-31G** basis [57] that includes polarization functions are very popular and are known to provide a good account of the energetics in many molecular systems. However, it is seen in Table 3 that these basis sets give carbon hfcc that are too large by more than a factor of two. Split valence basis sets have reasonable flexibility in the chemically important valence regions, but for spin density purposes they are overcontracted in the core region and do not allow for spin polarization of the carbon 1*s* shell that provides a large negative contribution [2, 11, 13] to the spin density at the carbon nucleus. An additional diffuse *s* function is also necessary in general [53] to adequately represent spin polarization in the valence region.

The split valence basis sets give hydrogen hfcc that are approximately correct. This is actually fortuitous, due again to a cancellation of errors [19]. Overcontraction of the hydrogen basis together with the absence of a diffuse *s*

Table 3. Hyperfine coupling constants in Gauss for several pi radicals[a] calculated with various basis sets

Method	$a(^{13}C_\alpha)$	$a(^{13}C_\beta)$	$a(^{1}H_\alpha)$	$a(^{1}H_\beta)$
		CH		
SCI/6-31G	35.4		−25.4	
SCI/6-31G**	35.1		−22.7	
SCI/[42|2]	13.0		−24.2	
SCI/[53|3]	22.9		−19.1	
SCI/(95|4)	10.2		−19.7	
SCI/[631|41]	13.0		−19.7	
Experiment	16.8[b]		−20.6[c]	
		CH_3 (planar)		
SCI/6-31G	63.2		−29.5	
SCI/6-31G**	71.4		−33.3	
SCI/[42|2]	31.1		−31.4	
SCI/[53|3]	41.6		−25.2	
SCI/(95|4)	30.4		−26.0	
SCI/[631|41]	26.6		−25.6	
Experiment	27[d]		−25[d]	
		C_2H_5 (planar)		
SCI/[42|2]	35.4	−16.8	−31.6	21.1
SCI/[631|41]	30.9	−14.9	−25.9	19.7
Experiment	(39.1)[e,f]	−13.6[e]	−22.4[g]	26.9[g]
		C_3H_5		
SCI/[42|2]	20.4	−21.6	−17.5, −18.4	2.9
SCI/[631|41]	18.0	−19.6	−14.1, −15.1	2.1
Experiment	21.9[b]	−17.2[h]	−13.9[h], −14.8[h]	4.2[h]

[a] The experimental [59] bond length of 1.1199 Å is used for CH radical. Geometries used for the other radicals are described in the footnotes to Table 2. Methyl and ethyl radicals are taken to be planar at the α-carbon

[b] Ref. [54]

[c] Ref. [55]

[d] Ref. [11]. See also footnote (b) of Table 1

[e] Ref. [42]

[f] The experimental [42] value of 39.1 G for the α-carbon in ethyl radical includes a significant vibrational averaging contribution from out-of-plane bending. SCI[631|41] calculations [38] estimate this to be ~8–9 G. Applying this calculated correction to the observed experimental result suggests that an "experimental" value of ~30–31 G would be more appropriate for comparison to calculations on planar ethyl radical

[g] Ref. [44]

[h] Ref. [46]

function leads to a significant overestimate of the spin population at hydrogen. But much of this overestimate is compensated by a significant underestimate of the amplitude of the *s* orbital at the nucleus, associated with the lack of a tight *s* function. The net result is a consistent modest overestimate of the hydrogen coupling.

From this discussion, it is clear that adequate representation of the carbon coupling requires some basis set flexibility in the outer core-inner valence regions, i.e., just as with valence regions, the core must also be given double zeta representation. Therefore, a full double zeta basis is the smallest reasonable set for hfcc determination, since each highly occupied orbital requires a partner spin polarization orbital that is localized in roughly the same region of space but is typically a little more diffuse. It should not be concluded that all double zeta and larger bases will provide satisfactory results, though. One that does is Dunning's [42|2] contraction [58] of the Huzinaga [50] (9*s*5*p*|4*s*) basis. It is seen in Table 3 that this basis generally overestimates the hfcc somewhat, but at least gives qualitatively correct results. The Dunning [53|3] contraction, despite being larger and more flexible, does not provide this cancellation as well and gives a poorer result for carbon. The fully uncontracted (9*s*5*p*|4*s*) basis has ample flexibility over the range it spans, but it is still not quantitatively reliable for spin density determination. Important effects not described by the fully uncontracted (9*s*5*p*|4*s*) basis require that it be augmented by diffuse *s* functions to describe the valence shell spin polarization, a tight *s* function on hydrogen as discussed above, and higher angular momentum functions to provide orbital polarization.

The errors found with the [42|2] basis, compared to the [631|41] results, are fairly systematic. They average about 10% high for carbon and about 20% high for hydrogen in the hfcc examples of Table 3. Use of the [42|2] basis in spin polarization calculations therefore appears reasonable for preliminary estimation of hfcc. A larger basis such as [631|41] is required for more accurate work.

5. Electron correlation

It should now be clear that the simple spin polarization model often provides a useful estimation of hfcc. But if high accuracy is desired, it will generally be necessary to go beyond this and include electron correlation effects. This is more computationally demanding, and consequently there is little information about how electron correlations affect spin densities.

It is well known that the two-electron charge density matrix Γ, together with its reduction to the one-electron charge density matrix, determines the total electronic energy and all charge density properties of a system. Less well known, and far from obvious, is the fact [60] that Γ also uniquely determines the one-electron spin density matrix, and therefore spin density properties such as hfcc. In fact, a simple explicit prescription has been given [60] for construction of the spin density matrix from Γ, which depends only on Γ being obtainable from a wave function that is a eigenfunction of the total spin operators S^2 and S_z. In some rough sense, one should therefore expect that introduction of electron correlation effects that "improve" Γ should also "improve" the spin density.

In this section we will consider the CH radical as a case study to examine the effects of electron correlation on hfcc. The wave function is dominated by the ROHF configuration, i.e., there are no important nondynamical correlation effects to complicate the situation, so this should be a typical representative of a wide variety of free radicals. Full configuration interaction (FULLCI) corresponds to including all possible configurations and represents the most complete calculation that can be carried out within a given basis set. One systematic procedure for approaching this limit is to start with the ROHF wave function and add to it single excitations (SCI), then also doubles (SDCI), triples (SDTCI), quadruples (SDTQCI), etc. Such results are shown for CH in Table 4. Ignore for the moment the results labelled MR(4)-SDCI, which will be described later.

Table 4. Hyperfine coupling constants in Gauss calculated for CH radical[a] with several basis sets including various levels of electron correlation

Wave function	[42|2]	[631|41]	[6321|421]
	$a(^{13}C)$ (experiment[b] = 16.7 ± 0.7)		
SCI	13.0	13.0	14.8
SDCI	15.3	8.9	10.7
MR(4) + SDCI	16.6	13.4	16.4
SDTCI	16.5	12.9	16.3
SDTQCI	16.6	13.1	
FULLCI	16.6		
	$a(^{1}H)$ (experiment[c] = -20.6 ± 0.1)		
SCI	−24.2	−19.7	−20.4
SDCI	−24.3	−19.1	−18.5
MR(4) + SDCI	−26.1	−21.2	−20.7
SDTCI	−26.0	−21.1	−20.7
SDTQCI	−26.1	−21.2	
FULLCI	−26.1		

[a] The experimental [59] bond length of 1.1199 Å is used in the calculations

[b] Ref. [54]

[c] Ref. [55]

With the double zeta [42|2] basis set it is seen that the results increase smoothly in magnitude with increasing excitation level. SCI provides a large fraction of the limiting results, SDCI gives a significant correction and SDTCI a smaller but still significant further correction. At this level the results are essentially converged to the SDTQCI and FULLCI results, which are identical to one another and are somewhat larger in magnitude than experiment.

However, the approach to high excitation levels is not monotonic for hfcc determined from larger basis sets. With the [631|41] basis that was developed for spin polarization (i.e., SCI) calculations, SDCI provides corrections to SCI that decreases the magnitude of both hfcc. SDTCI again increases the magnitude of the hfcc and is again essentially the same as the SDTQCI result, which presumably is essentially the same as FULLCI.

The studies just discussed are really only of academic interest, since such small basis sets are incapable of describing some of the physically important effects of electron correlation. Enlarging the basis to include more high angular momentum functions ($d_C = 1.12, 0.28; f_C = 0.56; p_H = 2.00, 0.50; d_H = 1.00$) produces a [6321|421] basis that should allow for a more realistic treatment of correlation effects. With this basis SDCI leads to a larger correction than seen before, which again makes the agreement with experiment worse for both nuclei, and again this is rectified by SDTCI. Although higher excitation calculations are not feasible with this basis, we see that SDTCI agrees quite well with experiment, and the smaller basis results make it plausible that inclusion of still higher excitations would not change the results much further. Apparently, then, double and triple excitations separately provide important contributions to the hfcc, but these are of opposite sign and tend to cancel one another, thereby collectively providing only a small net electron correlation correction to the SCI result.

More exaggerated behavior of this nature has been encountered in the case of H_2CN radical [37]. The large methylene hydrogen hfcc of ~ 90 G is due to roughly equal contributions of ~ 30 G each from direct, spin polarization, and electron correlation effects, whereas the carbon and nitrogen hfcc are dominated by just the spin polarization contributions. Just as in CH, with a large basis set capable of describing electron correlation it was found that including double excitations decreases the magnitude of all the hfcc and leads to somewhat worse agreement with experiment. The large errors at hydrogen compared to experiment were also attributed in that work to the effects of higher level excitations in the wave function.

Thus far we can say that while spin polarization (i.e., SCI) often, but not always, provides hfcc in fairly good agreement with experiment, corrections due to pair correlations (i.e., SDCI) are generally important. Triple excitations are also significant, although there is currently no evidence for qualitative importance of any higher excitations. Full SDTCI calculations are very expensive and it would be useful if it could be shown that only a subset of the triple excitations is responsible for providing the important hfcc contributions. We hypothesize that the important triple excitations are just double excitations from the spin-polarization singles.

It is feasible to test this hypothesis on CH radical. We first simulate the SCI calculation with a nearly equivalent but more compact wave function obtained by carrying out a four configuration SP-MCSCF calculation, including the dominant determinant and the three spin polarization configurations $\Psi^D_{1\sigma}$, $\Psi^D_{2\sigma}$ and $\Psi^D_{3\sigma}$, i.e., one for each of the highly occupied σ pairs. These four configurations are then used as the reference space for a multireference SDCI calculation, i.e., all single and double excitations with respect to any of the four reference configurations are included. This is referred to as MR(4)-SDCI in Table 4. Compared to a CI expansion based on the ROHF reference, it effectively contains all single and double excitations and the subset of triple excitations that corresponds to double excitations with respect to the spin polarization singles. With the [6321|421] basis, the total number of configurations is just 18% of that in full SDTCI and the correlation energy recovery corresponds to 46% of the distance from SDCI to SDTCI. Despite the much shorter configuration list, the results in Table 4 show that the MR(4)-SDCI calculation gives hfcc close to SDTCI.

Thus, the hypothesis appears true at least for CH radical. We have also obtained similar (unpublished) results for NH radical. The finding is also consistent with the fact that a UHF-based QCISD method [18] seems to perform quite well for hfcc. Since UHF itself effectively provides spin polarization single excitations, adding singles and doubles with respect to it brings in configurations that appear as triple excitations in a spin-restricted framework. The method also probably corrects for a major part of the spin contamination problem, as evidenced by that finding in closely related coupled cluster approaches [61]. It is therefore closely analogous to the MR-SDCI procedure described here.

If this hypothesis turns out to be true in general, then we have gained some valuable insight into why the simple spin polarization model often works well. It appears that double excitation corrections to hfcc due to pair correlations are important but often lead to much worse agreement with experiment. But triple excitations, that in some sense serve as spin polarization for the important pair correlations, are just as important and are often of opposite sign, tending to cancel the double excitation contributions. As a consequence, the simple spin polarization model often appears to work well even though it ignores these important effects. The methylene hydrogens in H_2CN radical seem to provide an example where this fortuitous cancellation does not occur and electron correlation corrections *in toto* are important. The systematic underestimation of β-hydrogen hfcc noted previously in spin polarization calculations on ethyl and allyl radicals may also be a result of failure of such cancellations of electron correlation effects.

This behavior leads to a caveat for practical CI calculations. It is easy enough for automated scanning procedures, such as are sometimes used to select the important configurations to be included in correlation calculations, to miss even some of the important first-order spin polarization effects. For example, the Ψ_{1s}^{D} configuration describing the $1s \rightarrow 1s^*$ single excitation for the core spin polarization on a first-row atom may typically [53] have a CI coefficient of only $\sim 10^{-3}$. If the effective $1s^*$ orbital is actually split up in practice among many virtual orbitals, then some important CI coefficients will be even smaller and could easily be missed. Any CI procedure for hfcc determination should therefore be forced to automatically include all Ψ_{k}^{D} type single excitation configurations. If, as we have argued in this section, the important triple excitations are related to higher-order mixed correlation-spin polarization effects, then configurations with extremely small coefficients may be important for the spin density. A means for including them must be found if configuration selection procedures are to be successful for hfcc determinations. The MR-SDCI procedure utilized here may provide a useful framework for approaching this problem.

6. Conclusion

A variety of points relating to spin density determination have been examined in this work, uncovering many instances of simple methods seeming to work better than they should. Here we provide a succinct summary of the more important findings.

Semiempirical procedures for hfcc determination that are based on spin polarization models often appear to work well. For example, the popular INDO method is often used for analyzing experimental hfcc. It gives reasonable results by virtue of adjusting parameter values to make up for important missing effects. It can be expected to work well only for radicals at or near their equilibrium geometries and with no unusual bonding situations.

Semiempirical calculations also sometimes fail, so more sophisticated *ab initio* approaches are required. The ROHF method describes the direct contributions to hfcc, although it does not treat the indirect spin polarization contributions that are of primary importance in pi radicals. The UHF method introduces spin polarization in an easily visualized manner, but spin contamination makes its use in computations controversial. Removal of the UHF spin contamination is also controversial. Careful evaluation of theoretical arguments and computational studies on the spin contamination question leads to the opinion that neither of these procedures can generally be depended upon for reliable results.

The spin-restricted SCI approach is free from these concerns and indicates that the spin polarization model is capable of reasonably estimating the hfcc in a variety of pi radicals, although β-hydrogen couplings seem to be systematically underestimated. A simple [42|2] double zeta basis set [58] gives fairly good spin polarization hfcc due to fortuitous cancellation of large errors, although this does not occur for many other common small basis sets. The differences found with a more suitable [631|41] basis specifically designed for hfcc determination appear systematic, so that the simpler [42|2] basis can be useful for preliminary spin polarization hfcc calculations.

Electron correlation effects are found to be significant. In particular, the good agreement with experiment often observed in SCI calculations is usually ruined when double excitations are included, provided the basis set is adequate for treating correlation effects. However, contributions from triple excitations are just as important as, or even more important than, those from double excitations and often tend to cancel them, with the result that the net electron correlation corrections appear small. Examination of the important triple excitations suggests that they can be regarded as describing spin polarization with respect to pair correlations. The systematic underestimation of β-hydrogen hfcc in spin polarization calculations appears be an example of these higher order electron correlation contributions not cancelling out.

In summary, the spin polarization model can provide a very useful simple tool for estimation of hfcc. For the radicals examined here, it gives satisfactory results for most of the hfcc, and the cases where it does not perform so well appear to be systematic enough to be predictable. It can also serve as a valuable initial step in more sophisticated approaches to spin density determination. These results are sufficiently encouraging that work is now in progress to delineate the general range of validity of the spin polarization model for larger systems.

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