On quantum-chemical estimates of constants of isotropic hyperfine coupling with protons in free radicals

N. D. Chuvylkin[a]* *and A. M. Tokmachev*[b]

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 4575

A scheme of consistent quantum-chemical calculations of constants of isotropic hyperfine coupling (IHFC) with protons ($a^{\rm H}_{\rm iso}$) in free radicals is considered for the case where the spin populations $\rho_s{}^{\rm H}$ are determined in the basic set of symmetrically orthogonalized atomic orbitals taking model σ- and π-electron fragments as an example. The competence of using two coefficients of proportionality K(H) when estimating the proton IHFC constants by semiempirical quantum-chemical methods was demonstrated. Theoretical substantiation of empirical values of the above coefficients previously used is revealed.

Key words: radiospectroscopy, ESR, free radicals, isotropic hyperfine coupling constants, magnetic moments of unpaired electron and protons; quantum-chemical calculations, basis set of symmetrically orthogonalized atomic orbitals.

Radiospectroscopic methods (ESR, NMR, ELDOR, ENDOR, CIDNP, ODMR, MODR, LMR, *etc.*[1]) serve as a valuable source of information on geometric and electronic structure of chemical compounds. However, only indirect information on the structural parameters of objects under study is contained in the spectral characteristics obtained by these methods. Therefore, a sequential theoretical interpretation of the experimentally recorded spectra in the framework of relevant adequate models is required.[2] In this case, the use of *ab initio* and semiempirical quantum-chemical methods makes it possible to appreciably enhance the informativity of radiospectroscopic investigations.[3]

Radiospectroscopic parameters are functions of the electron and spin distributions in molecular systems. However, the method of using general theoretical one-to-one correspondences between the measured and calculated values in particular computational schemes is problematical and requires a special consideration. In particular, the constants of isotropic hyperfine coupling (IHFC) in paramagnetic compounds, used in ESR spectroscopy, are determined from the relationship[4]

$$a^{Z_n}_{\rm iso} = K(Z)\cdot\rho_s{}^{Z_n}\ , \qquad (1)$$

where K(Z) is the coefficient of proportionality for each type of atoms Z and $\rho_s{}^{Z_n}$ is the spin population of the valence s-atomic orbital (AO) of a given atom Z_n. Previously,[3] it was suggested that to switch from the spin populations $\rho_s{}^{\rm H}$ employed in calculations by the semiempirical quantum-chemical UHF MNDO method to the IHFC constants $a^{\rm H}_{\rm iso}$, two coefficients of proportionality, $K(\mathrm{H}_\alpha)$ = 508 Oe (for $\rho_s{}^{\rm H} < 0$) and $K(\mathrm{H}_\beta)$ = 850 Oe (for $\rho_s{}^{\rm H} > 0$) should be used. This made it possible to smooth over the contradictions between recommendations of various authors who used either K(H) = 504.5 Oe [5] or K(H) = 850—900 Oe [6] in similar calculations of $a^{\rm H}_{\rm iso}$ constants for different types of free radicals.

Such a dependence of the coefficient of proportionality K(H) on the type of spin distribution can be correlated with the division[4] of most free radicals studied into two structurally representative symmetry classes, σ and π. The mechanism of spin density generation on the protons is dependent on the type of symmetry of the object: in purely σ-electron radicals, the IHFC with protons is mainly due to delocalization of the unpaired electron, resulting in positive spin populations, whereas the exchange spin polarization, which in most cases results in the appearance of negative spin densities on the protons, is responsible for the IHFC with magnetic nuclei in typical π-electron radicals. Despite such a quite logical explanation for the introduction of two coefficients of proportionality for hydrogen atoms in radical systems, particular K(H) values used in the framework of semiempirical methods need a theoretical substantiation for each mechanism of spin distribution.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 245—249, February, 1999.

1066-5285/99/4802-0245 $22.00

Coefficients of proportionality *K*(H) for a basis set of symmetrically orthogonalized AOs

As is known,[4] in the framework of the Hartree—Fock approximation without considering the spin-orbit interactions, the constant of IHFC between the magnetic moments of the unpaired electron and the proton can be expressed with a high accuracy using fundamental physical constants (the electron *g*-factor g_e, the Bohr magneton β_e, the Planck constant $\hbar$, and the proton gyromagnetic ratio γ_H) and the spin population $\rho_s{}^H$ of the $1s_H$ orbital of hydrogen atom:

$$a^H_{iso} = (8\pi/3)g_e\beta_e\hbar\gamma_H|s_H(0)|^2\rho_s{}^H. \qquad (2)$$

The use of the theoretical value:

$$\delta_H = (8\pi/3)g_e\beta_e\hbar\gamma_H|s_H(0)|^2, \qquad (3)$$

equal to 508 Oe, makes it possible to estimate spin populations of the 1s AO of H atoms in free radicals from experimental data on isotropic hyperfine splittings in ESR spectra. In this case, the s-AOs in the radicals are implied to be the same as those in isolated atoms.

However, there is reason to believe that the s-AOs of "the atoms in molecules" are somewhat changed. These changes, which are due to the influence of other atoms, should reflect the fact that the electron atomic clouds in a molecule are, as a rule, more compressed than in a free atom. Therefore, one can attempt to take into account this effect by varying the effective charges on the nuclei expressed using the orbital exponents ξ.

According to the results of *ab initio* calculations,[7] the 1s orbitals of H atoms in the molecules should be strongly changed, whereas the valence AOs of other atoms should be changed slightly. To a certain extent, this conclusion is also valid for free radicals. However, it should be emphasized that the optimum ξ^M values for the AOs in molecules are determined on the basis of variational principle and that optimization of AOs has a strong effect on the electron distribution and related properties, whereas varied total energies are much less sensitive to this procedure.

Taking into account that *ab initio* calculations of molecules are performed using Slater type orbitals (STO) whose shape differs from that of atomic orbitals and that variational procedure in each individual case is labor consuming, Pople at al.[8] introduced a set of standard values for the ξ^M parameters corresponding to an "average molecular environment" of the atoms. This set was obtained by averaging the optimum values for a number of small molecules. For H atoms in molecular systems, a value ξ_H of 1.24 was recommended.

From time to time, the problem of the necessity of using the modified STOs in semiempirical calculations has been discussed in the literature. Nevertheless, the standard STOs of the atoms from Li to Cl serve, as a rule, as basis sets in the most widely used semiempirical methods. A non-Slater type value ($\xi_H \cong 1.2$ *vs.* $\xi_H = 1$ according to Slater) is proposed only for the s-AO of hydrogen atom. At the same time, INDO calculations of the constants of IHFC with protons are performed using empirical δ_H values (Eq. (3)) to which ξ_H values of $\cong 1.02$ and $\cong 1.06$ correspond in the case of the a^H_{iso} constants in free radicals[9] and the constants of isotropic spin-spin coupling in molecules,[10] respectively. For other nuclei (Z $\neq$ H), the δ_Z values (Eq. (3)) also differ from the Hartree—Fock type values for free atoms[11] and the δ_Z [9,10] and ξ_Z [8] values tend to be changed in opposite directions.

Such an inconsistency can be associated with the fact that the behavior of the Ψ-function only in the region immediately adjacent to the nucleus is significant for calculations of the IHFC constant. Small changes in the values of the Ψ-function in this region virtually have no effect on the total energy, whereas they strongly affect the constant of IHFC with a given nucleus. It is likely that the use of empirical δ_Z values makes it possible to more adequately describe both the behavior of the Ψ-function in the vicinity of the nuclei in radicals and molecules and additional effects caused, *e.g.*, by neglect of the overlap or by drawbacks in the calculations of the spin density in the framework of the UHF scheme.

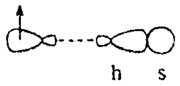
A key role in the development of a possibly more rigorous mathematical formalism of new quantum-chemical approaches has always been assigned to the choice of the basis set. As is known,[12] the zero differential overlap (ZDO) approximation, which still is widely used, was theoretically substantiated in the basis set of symmetrically orthogonalized AOs localized mainly in different space regions. Taking into account all of the above and the fact that conventional s-, p-, and d-AOs (despite they are orthogonal in symmetry) are localized mainly in the same spherically symmetric region, the use of a basis set of hybrid AOs seems to be rather fruitful.

The hybrid h-AOs of the same center are not only orthogonal, but are also localized in different spatial regions, *i.e.*, they meet ZDO conditions. For this reason, such AOs are, on the one hand, adequate to symmetrically orthogonalized AOs and, on the other hand, they are closely related to conventional chemical concepts. Of course, the hybrid h-AOs of different centers and, first of all, those corresponding to a chemical bond, are not orthogonal; however, they can be orthogonalized using a specially developed procedure.[13]

Unfortunately, the choice of the hybrid basis set is ambiguous and it indubitably constrains the field of application of the method. It is the most natural to use the method of hybrid basis set for the systems composed of a skeleton formed by C atoms of a given hybridization, to which heteroatoms are bonded. It should be noted that similar systems are most typical in organic chemistry and biochemistry. One of the calculation procedures consists in determining the required parameters for the hybrid AOs of small molecules and their further application to large systems. The quantitative *ab* *initio* calculations of a number of molecules with the hybrid basis set of AOs [14] indicate that the wave functions and energies obtained in this case are in good agreement with those found in the Hartree—Fock approximation.

Taking into account all of the above, let us consider first the formalism of calculations of the constants of IHFC with protons in a typical σ-electron radical whose model fragment is shown in Scheme 1. To a first approximation, small overlaps of hybrid h-AOs that do not correspond to a chemical bond can be neglected[4] on going to the basis set of AOs symmetrically orthogonalized according to Löwdin. In other words, it is sufficient to focus our attention only on one C—H σ-bond formed from a hybrid h-AO of the C atom and the 1s-AO of the H atom (see Scheme 1). Let the overlap integral $S_0 = \langle s|h \rangle$ correspond to these two non-orthogonal AOs. Let us use them to construct two new orthonormalized AOs, $\bar{s}$ and $\bar{h}$, by the Löwdin procedure of symmetrical orthogonalization.

Scheme 1



When the overlap matrix has the form

$$O = \begin{pmatrix} 1 & S_0 \\ S_0 & 1 \end{pmatrix}, \qquad (4)$$

the reciprocal matrix can be written as

$$O^{-1} = \frac{1}{1 - S_0^2}\begin{pmatrix} 1 & -S_0 \\ -S_0 & 1 \end{pmatrix}. \qquad (5)$$

Let us find the $O^{-1/2}$ matrix using the notations

$$O^{-1/2} = \begin{pmatrix} A & B \\ B & A \end{pmatrix}. \qquad (6)$$

By multiplying the matrices, $O^{-1/2} \cdot O^{-1/2} = O^{-1}$, and equating the corresponding matrix elements we get the following system of equations

$$\begin{cases} A^2 + B^2 = 1/(1 - S_0^2) \\ 2AB = -S_0/(1 - S_0^2) \ . \end{cases} \qquad (7)$$

By adding these equations and subtracting the second equation from the first we get the system

$$\begin{cases} A + B = \pm\left(1/\sqrt{1 + S_0}\right) \\ A - B = \pm\left(1/\sqrt{1 - S_0}\right) \ . \end{cases} \qquad (8)$$

Without loss of generality, let us set:

$$\begin{cases} A = 1/2\left[\left(1/\sqrt{1 + S_0}\right) + \left(1/\sqrt{1 - S_0}\right)\right] \\ B = 1/2\left[\left(1/\sqrt{1 + S_0}\right) - \left(1/\sqrt{1 - S_0}\right)\right] \end{cases} \qquad (9)$$

and represent the symmetrically orthogonalized AOs as follows:

$$\begin{cases} \bar{h} = Ah + Bs \\ \bar{s} = As + Bh \ . \end{cases} \qquad (10)$$

If the molecular orbital (MO) of the unpaired electron is expressed as a linear combination of AOs symmetrically orthogonalized according to Löwdin, then the square of the coefficient at the hydrogen s-AO (the one-electron contribution $\rho^0{}_{H}$ to the spin population of the AO of H atom) will be

$$\rho^0_H = (c_s \cdot A + c_h \cdot B)^2, \qquad (11)$$

where c_s and c_h are the coefficients at corresponding orthonormalized AOs in which this MO is expanded. Because of alternation of the damping factor of the one-electron contribution to the spin density in typical σ-electron radicals,[4,15,16] the c_h coefficient is close to zero and we can write for $\rho^0{}_H$:

$$\rho^0_H = c_s{}^2 \cdot \xi_H{}^3, \qquad (12)$$

where

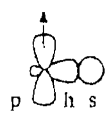
$$\xi_H = A^{2/3}. \qquad (13)$$

In typical cases, deviations from $S_0 \approx 0.75$ are small; according to Eq. (13), this corresponds to a ξ_H value of ≈ 1.23. It should be noted that an analogous scheme was also used previously;[4] however, expansions in power series in S_0 with truncation of terms of the fifth $(S_0{}^5)$ and higher orders were used instead of analytical expressions. Because of such truncation, under the same conditions the ξ_H factor appeared to be underestimated by 0.04.

Thus, in accordance with relationships (1)—(3) and (12), the Hartree—Fock coefficient of proportionality (δ_H = 508 Oe) should be modified. Taking ξ_H = 1.23, we get $508 \cdot \xi_H{}^3 \approx 950$ Oe, *i.e.*, almost the same value as that used previously[3,6] for σ-electron radicals. It is in this basis set of symmetrically orthogonalized AOs that the ZDO approximation is considered to be well substantiated theoretically.[12] From this it follows that in numerous semiempirical quantum-chemical variants of the NDO scheme (CNDO, INDO, MINDO, MNDO, AM1, PM3, *etc.*), the constants of IHFC with protons, that in typical σ-electron radicals are mainly due to spin delocalization, should be calculated using larger values of the coefficient of proportionality $K(H_\beta)$ compared to the Hartree—Fock value.

On the contrary, in a purely π-electron radical whose model fragment is shown in Scheme 2, the IHFC with proton is completely determined by the exchange spin polarization that appears when taking into account the σ—π-configuration interaction.

Scheme 2



First we consider this fragment in the valence bond approximation. Let us construct the normalized doublet wave function $\Psi_0^{(0)}$ of the ground state from a conventional p_π-AO, symmetrically orthogonalized $\bar{s}$ and $\bar{h}$ AOs, and the spin functions α and β using a standard antisymmetrizer **A**.

$$\Psi_0^{(0)} = \mathbf{A}\,\frac{1}{\sqrt{2}}\,\mathrm{p}\bar{\mathrm{h}}\bar{\mathrm{s}}(\alpha\alpha\beta - \alpha\beta\alpha). \qquad (14)$$

Then, the excited doublet state of the same configuration is described by the function:

$$\Psi_1^{(0)} = \mathbf{A}\,\frac{1}{\sqrt{6}}\,\mathrm{p}\bar{\mathrm{h}}\bar{\mathrm{s}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha). \qquad (15)$$

At the first-order level of perturbation theory ($|\lambda| \ll 1$), mixing of these two functions yields a refined wave function of the ground state of the radical fragment:

$$\Psi_0^{(1)} = \Psi_0^{(0)} + \lambda\Psi_1^{(0)}, \qquad (16)$$

The expression for λ has the form

$$\lambda = -(H_{01}/\Delta E_{0\to 1}), \qquad (17)$$

where ΔE is the difference between the energies of the states under consideration and H_{01} is the matrix element of the electron Hamiltonian, taken between the $\Psi_0^{(0)}$ and $\Psi_1^{(0)}$ functions. With regard to relations (9), the latter is reduced to the "scaled" difference of conventional exchange integrals $K_{\mu\nu}$ of interelectron interaction:

$$H_{01} = \frac{1}{\sqrt{3}}\left(K_{\mathrm{p}\bar{\mathrm{s}}} - K_{\mathrm{p}\bar{\mathrm{h}}}\right) =$$

$$= \frac{1}{\sqrt{3}}\left[\langle \mathrm{p}(A\mathrm{s}+B\mathrm{h})|(A\mathrm{s}+B\mathrm{h})\mathrm{p}\rangle - \langle \mathrm{p}(A\mathrm{h}+B\mathrm{s})|(A\mathrm{h}+B\mathrm{s})\mathrm{p}\rangle\right] =$$

$$= \left(K_{\mathrm{ps}} - K_{\mathrm{ph}}\right)/\sqrt{3(1 - S_0^2)}\,. \qquad (18)$$

Starting from the general formula:[4]

$$\rho(\vec{r}) = \left\langle \Psi \middle| S_z^{-1} \sum_k \hat{S}_z(k)\cdot\delta(\vec{r}_k - \vec{r}) \middle| \Psi \right\rangle, \qquad (19)$$

(where $\delta(\vec{r}_k - \vec{r})$ is the Dirac δ-function and summation is performed over all electrons of the paramagnetic system with an average value of the projection of the spin angular moment on the z axis of S_z), one can easily obtain the expression for the spin density ρ(0) on a proton, related to the complete wave function (16) of the three-electron fragment (see Scheme 2):

$$\rho_{\mathrm{H}}(0) = -\left(2\lambda/\sqrt{3}\right)\left[|\bar{\mathrm{s}}(0)|^2 - |\bar{\mathrm{h}}(0)|^2\right] =$$

$$= -\left(2\lambda/\sqrt{3}\right)\left(A^2 - B^2\right)|\mathrm{s}(0)|^2 =$$

$$= -\left(2\lambda/\sqrt{3(1-S_0^2)}\right)|\mathrm{s}(0)|^2. \qquad (20)$$

Then, taking into account relations (2), (3), (17), (18), and (20), we finally get in the framework of the employed version of the valence bond method:

$$(a_{\mathrm{iso}}^{\mathrm{H}})_{\mathrm{VB}} = -\frac{2}{3(1 - S_0^2)}\cdot\frac{K_{\mathrm{ph}} - K_{\mathrm{ps}}}{\Delta E_{0\to 1}}\,\delta_{\mathrm{H}}\,. \qquad (21)$$

Comparison of expression (21) with that given by McConnell[17] shows that they differ from each other only in the factor $(2/3)(1 + S_0^2)$ that is close to unity at $S_0 = 0.75$. Hence, virtually no change in the Hartree—Fock coefficient of proportionality (δ_{H} = 508 Oe) between the estimated IHFC constant $a_{\mathrm{iso}}^{\mathrm{H}}$ and the spin population ρ_s^{H} of the hydrogen atom calculated in the ZDO approximation is required when passing to a symmetrically orthogonalized basis set in the case of hydrocarbon aromatic and conjugated π-electron radicals.

When considering the exchange spin polarization in a model three-electron fragment (see Scheme 2) in the framework of molecular orbital theory, it is necessary to construct bonding and antibonding MOs from symmetrically orthogonalized $\bar{s}$- and $\bar{h}$-AOs:

$$\sigma = \left(1/\sqrt{2}\right)\left(\bar{\mathrm{s}} + \bar{\mathrm{h}}\right), \qquad (22)$$

$$\sigma^* = \left(1/\sqrt{2}\right)\left(\bar{\mathrm{s}} - \bar{\mathrm{h}}\right). \qquad (23)$$

Using Eqs. (9) and (10), these MOs can be written in conventional[17] form:

$$\sigma = \frac{A+B}{\sqrt{2}}(\mathrm{s} + \mathrm{h}) = \frac{1}{\sqrt{2(1+S_0)}}(\mathrm{s} + \mathrm{h}), \qquad (24)$$

$$\sigma^* = \frac{A-B}{\sqrt{2}}(\mathrm{s} - \mathrm{h}) = \frac{1}{\sqrt{2(1-S_0)}}(\mathrm{s} - \mathrm{h}). \qquad (25)$$

This means that in the approximation used, the expression for IHFC constant $a_{\mathrm{iso}}^{\mathrm{H}}$ remains unchanged on going from overlapped AOs to symmetrically orthogonalized AOs. Thus, semiempirical quantum-chemical analysis of the constants of IHFC with protons in π-electron radicals by both molecular orbital theory and the alternative valence bond theory should be performed using the Hartree—Fock coefficient of proportionality (δ_{H} = 508 Oe).

In conclusion, it should first of all be emphasized that the above consideration of simplified models not only demonstrated the validity of using[3,5,6] two coefficients of proportionality $K(H)$ in relationship (1) in calculations of the constants of IHFC with protons by most widely employed semiempirical quantum-chemical methods, but also showed the theoretical substantiation of the empirical values of these coefficients used previously. It should be noted that the conclusions drawn when considering the model π-fragment (see Scheme 2) are valid for the vast majority of planar π-electron radicals (with both carbon and heteroatomic radical center) since the IHFC constants are entirely determined by the only mechanism of π—σ-exchange spin polarization.[4] At the same time, relationship (12), which has the same level of theoretical substantiation, is convenient in practice, and obtained by the use of equally simplified σ-fragment (see Scheme 1), can be inadequate for the description of some σ-electron radicals. In particular, this can be due to uncertainties in the AO hybridization (especially, for heteroatoms, *e.g.*, B, N, and O) and the superposition of the delocalization and spin polarization effects that often have comparable values and act in opposite directions.

References

1. H. Fisher, F. A. Neugebaer, and A. Berndt, *Magnetic Properties of Free Radicals*, Landolt—Börnstein, New Series II, **17-b/c**, Berlin, 1987.
2. N. D. Chuvylkin, A. M. Tokmachev, A. V. Fionov, and E. V. Lunina, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1743 [*Russ. Chem. Bull.*, 1997, **46**, 1649 (Engl. Transl.)].
3. N. D. Chuvylkin, I. Yu. Shchapin, V. L. Klochikhin, V. A. Tikhomirov, and V. I. Fel'dman, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1992, **33**, 307 [*Bull. Moscow Univ., Ser. 2, Chem.*, 1992, **33** (Engl. Transl.)].
4. G. M. Zhidomirov, P. V. Schastnev, and N. D. Chuvylkin, *Kvantovo-khimicheskie raschety magnitno-rezonansnykh parametrov* [*Quantum-Chemical Calculations of Magnetic Resonance Parameters*], Nauka, Novosibirsk, 1978, 368 pp. (in Russian).
5. P. Bischof and G. Friedrich, *J. Comp. Chem.*, 1982, **3**, 486.
6. C. Glidewell, *J. Chem. Soc., Perkin Trans. 2*, 1983, **8**, 1285.
7. R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
8. W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 2769.
9. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, 1968, **90**, 4201.
10. J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, 1968, **49**, 2965.
11. P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals. An Application of Electron Spin Resonance to the Study of Molecular Structure*, Elsevier, Amsterdam, 1967.
12. R. D. Brown and K. R. Roby, *Theor. Chim. Acta*, 1970, **16**, 175.
13. P.-O. Löwdin, *J. Chem. Phys.*, 1950, **18**, 365.
14. J. D. Petke and J. L. Whitten, *J. Chem. Phys.*, 1969, **51**, 3166.
15. N. D. Chuvylkin, Ph. D. (Chem.) Thesis, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1972, 206 pp. (in Russian).
16. N. D. Chuvylkin and A. M. Tokmachev, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1575 [*Russ. Chem. Bull.*, 1997, **46**, 1501 (Engl. Transl.)].
17. H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

Received March 25, 1998;
in revised form June 16, 1998