

Systematic estimation of isotropic hyperfine coupling constants for protons in free radicals

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Modified formalism of consistent quantum-chemical estimations of contact interactions between magnetic moments of an unpaired electron and protons, when the spin populations of atoms are determined in the basis of symmetrically orthogonalised atomic orbitals, is presented and examined using the H₂C=CH· test free radical as an example.

Radiospectroscopic investigations provide a wealth of information on the structures of molecular compounds. Thus, a simple EPR technique is widely used for studying radical systems. Experimental EPR spectra are often difficult to interpret.¹ Current methods of quantum chemistry can give useful assistance in identifying spectra.^{2–5} Successful applications of these approaches require reliable techniques for computation of magnetic resonance parameters of radical systems.

Bulky radical systems are of current practical interest. Thus, radical probes such as 2,2,6,6-tetramethylpiperidin-*N*-oxyl and 2-octyl-2,4,5,5-tetramethyl-3-imidazolin-*N*-oxyl at the surfaces of various catalysts were systematically examined.⁶ Analogous radical probes were added to protein molecules for investigating their conformational transformations.⁷ The commonly used *ab initio* methods even of relatively low levels are usually inapplicable in practice to these bulky systems because of technical difficulties. In the circumstances, alternative quantum-chemical approaches to estimate the EPR spectra parameters of free radicals deserve special consideration. The reliable and rapid identification of highly informative EPR spectra is presently associated, as a rule, with the future progress and applications of the density functional theory^{8–11} or adequate semi-empirical quantum-chemical ZDO approaches,^{2,3,12,13} which are believed to be theoretically well-founded in the basis of Löwdin symmetrically orthogonalised atomic orbitals (AOs).¹⁴

In the framework of semi-empirical ZDO approaches, when establishing structure-property correlations, the confusing problems of ascertaining the interrelations between the calculated wave functions and experimental radiospectroscopic parameters inevitably arise. Thus, to relate the isotropic hyperfine coupling (ihfc) constant $a_{\text{iso}}^{Z_n}$ found by EPR to the quantum-chemically calculated spin population $\rho_{s_n}^{Z_n}$ of a valence *s*-AO of the particular *n*-th atom Z_n , the following well-known expression is commonly used:²

$$a_{\text{iso}}^{Z_n} = K(Z)\rho_{s_n}^{Z_n} \quad (1)$$

Over a long period of time it was assumed that the proportionality coefficient $K(Z)$ in this expression was dependent on only the type of the atom regardless of its chemical environment, *i.e.*, of the compound in which it occurred.

However, afterwards in calculations of proton ihfc constants by ZDO semi-empirical methods tremendously unlike values of the proportionality coefficient $K(H)$ were suggested.^{15,16} Keeping this in mind, the opinion was expressed³ that for description of two fundamentally alternate mechanisms of spin density distribution (*i.e.*, polarization and delocalization) the use of two corresponding highly different $K(H)$ and $K(H)$ values was reasonable. Regardless of the qualitative explanation³ of a need for using two proportionality coefficients $K(H)$ and $K(H)$, which diminishes the contradiction between recommendations of different authors,^{15,16} it was necessary to determine theoretically each of the coefficients using an adequate mathematical expression that takes into account the specificity of both mechanisms of spin distribution and conventional quantum-chemical approximations.

Recently, using model π - and σ -electron hydrocarbon fragments as an example, the scheme of consistent quantum-chemical calculations of the proton ihfc constants $a_{\text{iso}}^{\text{H}}$ for free radicals was considered,¹² when the spin populations ρ_s^{H} were determined in the basis of Löwdin symmetrically orthogonalized AOs. Keeping in mind the fact that in a purely π -electron radical the ihfc with a proton results only from the exchange spin polarization, the expression was deduced in the framework of a valence bond (VB) approach with the inclusion of π - σ configuration interaction:

$$K(H) = \delta(H) \frac{2}{3} (1 + S_{hs}^2), \quad (2)$$

where $\delta(H)$ is the Hartree–Fock value (508 G) of the proportionality coefficient, and S_{hs} is the overlap integral of a hybrid *h*-AO of a heavy atom (C) and 1*s*-AO of an H atom. From equation (2) it follows that for $S_{hs} \approx 0.75$ (typical case) the values of the $K(H)$ and $\delta(H)$ are practically indistinguishable. At the same time, it was shown¹² that in the framework of the MO LCAO theory when passing from overlapping AOs to symmetrically orthogonalized AOs the expression for the ihfc constant $a_{\text{iso}}^{\text{H}}$ did not undergo any changes in the case of π -electron radicals.

At the same time, it was established¹² that the ihfc constants for protons in typical π -electron radicals, resulting predominantly from spin delocalization, were to be computed with the proportionality coefficient $K(H)$ higher than the Hartree–Fock coefficient because its expression with even reduced account of only the one-electron contribution ρ_{H}^0 into the spin population of hydrogen 1*s*-AO assumed the substantially modified form in the basis of symmetrically orthogonalized AOs:

$$K(H) = \delta(H) \left[\frac{1}{2} \left(\frac{1}{\sqrt{1-S_{hs}}} + \frac{1}{\sqrt{1+S_{hs}}} \right) \right]^2. \quad (3)$$

For typical values of the overlap integral S_{hs} the proportionality coefficient $K(H)$ is within the range 700–800 G. This

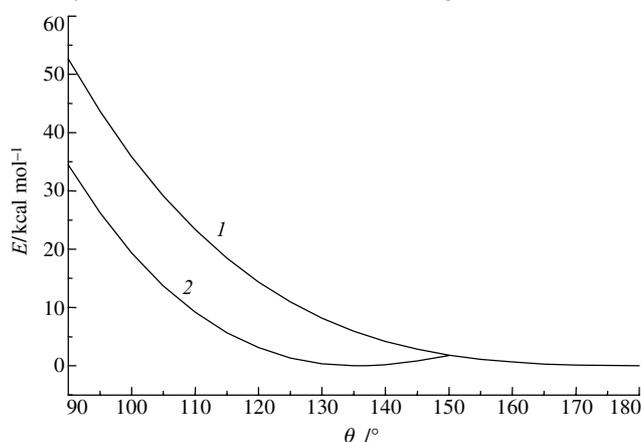


Figure 1 Relative total energies of the vinyl π -electron radical as functions of the angle CCH : (1) MNDO/UHF, (2) UHF/6-31G**.

is consistent with the data of ref. 17 wherein it has been found that the best coincidence of semi-empirically calculated ihfc constants and experimental ones for protons of a number of -radicals is observed when $K(H) = 743$ G.

With the use of the restricted Hartree–Fock (RHF) method, the calculated one-electron spin densities ${}^{\text{RHF}}\rho^0(\vec{r})$ are always not negative whereas real physical experiments also detect the negative total spin densities $\rho(\vec{r})$. The appearance of negative $\rho(\vec{r})$ values is owing to the additional polarization contribution $\rho^{\text{P}}(\vec{r})$ caused mainly by exchange electronic correlation.² This correlation suggests that the electrons with different spins become differently distributed in the space.

In practical quantum-chemical calculations of magnetic resonance parameters of free radicals with allowance for electron correlation effects, the UHF method is most widely used. In this method, the one-electron (delocalization) and polarization contributions to the spin density are not partitioned.² Note that because of proper symmetry properties of wave functions the polarization component $\rho^{\text{P}}(\vec{r})$ is usually overestimated in UHF calculations.

The separation of the UHF spin densities into the delocalization and polarization contributions is possible by the natural orbital analysis within the scope of UHF method.^{2,18,19} At the same time, a simple relation between the UHF and projected unrestricted Hartree-Fock (P UHF) wave functions is well known.^{18,19} From these considerations a simple way was found to partition the spin density calculated by the UHF method into contributions from the spin polarization and spin delocalization mechanisms. For doublet radicals, the polarization correction takes the form:¹⁸

$${}^{\text{UHF}}\rho^{\text{P}}(\vec{r}) = \frac{3}{2} [{}^{\text{UHF}}\rho(\vec{r}) - {}^{\text{PUHF}}\rho(\vec{r})] \quad (4)$$

The delocalization contribution is then approximated as the difference:

$${}^{\text{UHF}}\rho^0(\vec{r}) = {}^{\text{UHF}}\rho(\vec{r}) - {}^{\text{UHF}}\rho^{\text{P}}(\vec{r}) \quad (5)$$

The validity of this approach was confirmed¹⁸ by comparing the delocalization components ${}^{\text{UHF}}\rho^0$ calculated by equation (5) with those (${}^{\text{RHF}}\rho^0$) obtained by the open-shell RHF method.² The result is that equation (5) becomes:

$${}^{\text{UHF}}\rho(\vec{r}) - {}^{\text{RHF}}\rho^0(\vec{r}) = {}^{\text{UHF}}\rho^{\text{P}}(\vec{r}) \quad (6)$$

Because of the physical simplicity, equation (6) can be quite useful in systematic analysis of the ihfc constants for protons in bulky radical systems. In the case of the RHF approach (e.g., CNDO/SP variant²) the polarization correction is estimated, as a rule, with the use of the perturbation theory.

For convenience, we used expression (6). However, it was taken into account that the polarization component $\rho^{\text{P}}(\vec{r})$ of the total spin density can be partitioned into contributions of so-called spin [$\rho^{\text{SP}}(\vec{r})$] and exchange [$\rho^{\text{EP}}(\vec{r})$] polarizations,² and the component $\rho^{\text{EP}}(\vec{r})$ is the only one for -radicals and much more significant than $\rho^{\text{SP}}(\vec{r})$ for -radicals. Consequently, supposing the correction ${}^{\text{SP}}\rho_s^{\text{H}}$ to be negligible for -radicals and not entering into a contradiction with the results,¹² we have, when estimating the polarization contribution ${}^{\text{P}}a_{\text{iso}}^{\text{H}}$ with equation (1), to multiply the spin population ${}^{\text{P}}\rho_s^{\text{H}}$ obtained using equation (6) by the Hartree-Fock proportionality coefficient $K(H) = 508$ G.

Table 1 Bond lengths (Å) and angles (°) in the vinyl radical, optimised by semi-empirical and *ab initio* methods.

Parameter	Method	
	MNDO	6-31G**
CH	1.049	1.070
CH _{cis}	1.091	1.075
CH _{trans}	1.091	1.078
CC	1.307	1.341
CCH	180.0	135.6
CCH _{cis}	122.9	121.4
CCH _{trans}	122.9	122.0

With the aim to test the presented approach to evaluating the ihfc constants for protons, in the framework of the MNDO approximation,²⁰ we consider the vinyl radical, which is commonly regarded as a 'criterion'.^{2,3,17,18} This approach based on equations (1)–(3) and (6), the standard MNDO parametrization, and the Dewar half-electron method²¹ is below referred to as MNDORU.

When the geometry of free radicals is inadequately known, the magnetic-resonance parameters are evaluated by quantum-chemical methods with great errors.³ Unfortunately, experimental data on the geometry of free radicals are either absent at all or often ambiguous.² At the same time, because of the high sensitivity of calculated magnetic-resonance characteristics to changes in the structural parameters and the ability of NDO approaches to interpret radiospectroscopic data with acceptable accuracy, if the supposed structures of free radicals are close to the real ones, these methods make it possible to predict the electronic structure and geometry of free radicals more exactly than an energy optimization procedure.³

Like the majority of other radicals, the geometry parameters of a vinyl radical were not determined experimentally. Table 1 contains these parameters computed by us using both semi-empirical MNDO and *ab initio* methods in the 6-31G** basis. The two sets of structural characteristics are similar; however, the data for the CCH angle are dramatically different. The procedure of energy variation can reliably determine the gas-phase geometries of free radicals only at a level of non-empirical calculations in extended basis sets in quality comparable to the 6-31G** basis. Therefore, we can believe that real structural parameters of the vinyl radical are closer to the *ab initio* calculated data (Table 1).

Table 2 includes, together with the experimental $a_{\text{iso}}^{\text{H}}$ values, the delocalization (${}^0a_{\text{iso}}^{\text{H}}$) and spin-polarization (${}^{\text{P}}a_{\text{iso}}^{\text{H}}$) contributions and total ($a_{\text{iso}}^{\text{H}} = {}^0a_{\text{iso}}^{\text{H}} + {}^{\text{P}}a_{\text{iso}}^{\text{H}}$) ihfc constants estimated according to the above scheme for the specified (*ab initio* optimised) radical geometry. As can be seen, the MNDO/RHF method did not reproduce the recorded ihfc constants for the protons in the vinyl radical even qualitatively. After taking into account the polarization contribution, the great discrepancies between theoretical and experimental values for *cis*- and *trans*-protons became much lower, but for the proton H calculated ihfc constant was found to have a wrong sign. It is problematic that the reversed sign [$a_{\text{iso}}^{\text{H}}(\text{H}) = -1.3$ G] was also obtained in *ab initio* calculations, whereas the INDO and CNDO/SP methods led to a satisfactory quantitative description of this constant [$a_{\text{iso}}^{\text{H}}(\text{H}) = 10.7$ G and $a_{\text{iso}}^{\text{H}}(\text{H}) = 13.4$ G, respectively].²²

The contradiction with the experiment can be removed by a change in geometry parameters. Taking into account the data in Table 1, it is reasonable to remove the strong discrepancy between the calculated and experimental values by variation of the valence angle $\text{CCH} \equiv \theta$ keeping in mind the pronounced angular dependence of the calculated ihfc constant for the -proton in the vinyl radical.^{2,3,17} The remaining (more 'rigid') structural parameters may be fixed in the course of this variation.

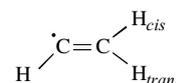
Relative total energies of the vinyl radical calculated by MNDO/UHF and UHF/6-31G** methods are plotted in Figure 1 as functions of angle θ . As can be seen in Figure 1 (curve 1),

E remains practically constant over a wide range of θ . Hence, it is reasonable to accept the degree of agreement of theoretical

Table 2 Experimental data²³ and theoretical quantities^a estimated for *ab initio* optimised radical geometry.

Nucleus	S_{hs}	$K(H)$	MNDORU			Exp.
			${}^0a_{\text{iso}}^{\text{H}}$	${}^{\text{P}}a_{\text{iso}}^{\text{H}}$	$a_{\text{iso}}^{\text{H}}$	$a_{\text{iso}}^{\text{H}}$
H	0.661	791	28.3	-31.4	-3.1	13.4
H _{cis}	0.648	773	18.3	12.2	30.6	37.0
H _{trans}	0.649	774	52.6	9.2	61.8	65.0

^aEquations (1)–(3).



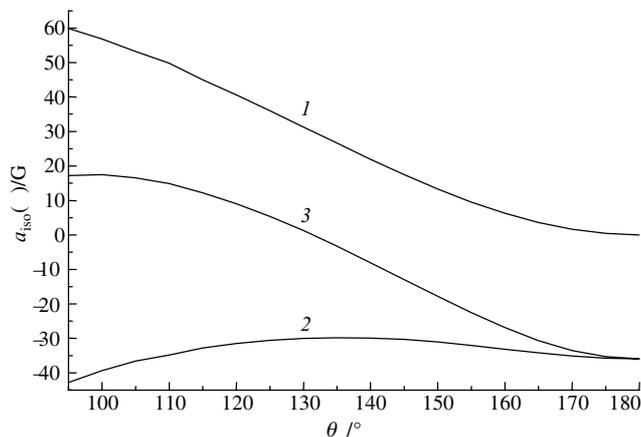


Figure 2 Delocalization (1) and spin-polarization (2) contributions and the total (3) ihfc constant for the β -proton in the vinyl β -electron radical as functions of the angle CCH.

and experimental magnetic-resonance parameters for one or another radical geometry as an adequate test of authenticity of the vinyl radical geometry.

Figure 2 depicts the calculated angular dependence of one-electron (curve 1) and spin-polarization (curve 2) components and the total ihfc constant (curve 3) for the vinyl β -radical. Curve 3 in Figure 2 decays monotonically as the varied angle increases, whereupon a fair agreement with the experiment is achieved for $\theta \approx 110\text{--}125^\circ$ rather than $\theta \approx 135^\circ$. The former value is energy-acceptable (Figure 1) and permissible from the point of view of computing errors of the *ab initio* method²⁴ and a possible matrix effect on the constant under discussion. Anyhow, the θ angle estimated roughly in this manner proved to be much closer to the *ab initio* calculated one than the θ angle optimised by the MNDO/UHF method. The evaluated ihfc constants for the *cis*- and *trans*-protons distant from the radical centre in the vinyl radical range from 23.8 to 27.1 G and from 62.1 to 61.8 G at $\theta \approx 110\text{--}125^\circ$, respectively. Therefore, with the account of spin polarization in the MNDORU approximation, all above experimental values of ihfc constants can be, in principle, reproduced with the use of geometry parameters of the vinyl radical, which are different only slightly from those fully optimised by us with the UHF/6-31G** method and accepted as authentic (Table 1). The same has been recently demonstrated¹³ by the results of similar MNDORU calculations carried out for a test representative sample of 17 β - and α -electron free radicals.

Thus, the modified scheme¹² of logically consistent quantum-chemical calculation of ihfc constants for protons in free radicals when the spin populations of atoms are determined in the basis of Löwdin symmetrically orthogonalised $\overline{\text{AO}}$ s quite naturally removes the seeming contradiction in the applications^{15,16} of two tremendously different proportionality coefficients in equation (1) for estimating these constants by most commonly used semi-empirical methods of quantum chemistry. We can also conclude that in calculations of ihfc constants for protons even in β -electron radicals the spin-polarization effects must be

borne in mind. Reliable determinations of geometry parameters of free radical systems by modern quantum-chemical methods require not only findings of a minimum on the potential energy surface but also concurrent comparisons of theoretical and experimental radiospectroscopic characteristics.

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