Evaluation of MNDO approximation in quantum-chemical calculations of anisotropic hyperfine coupling tensors in free radicals

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The MNDO approximation was tested for applicability in quantum-chemical calculations of anisotropic hyperfine coupling tensors using the same set of 17 free radicals as that used previously in evaluating a new procedure for quantum-chemical estimates of constants of isotropic hyperfine coupling with protons in the framework of the same approach.

Key words: ESR, free radicals, anisotropic hyperfine coupling constants, quantum-chemical calculations.

Solid-state ESR spectra of free radicals contain a greater body of information on their electronic and molecular structure as compared to liquid-phase ESR spectra. For instance, they make it possible to determine the relative signs and magnitudes of magnetic resonance parameters as well as the directions of the vectors of interaction between the magnetic moments of the unpaired electron and nuclei.[1–6] The most reliable are the results obtained in studies of single crystals, since in these cases different orientations of the same free radicals are related by symmetry operations. Unfortunately, in some instances attempts to grow single crystals fail. In addition, many objects (*e.g.*, polymers) cannot be obtained as single crystals.

The observed ESR spectra of radicals with random orientations in polycrystalline matrices often can hardly be interpreted.[5] Liquid-phase ESR spectra become significantly simplified because of effective averaging of anisotropic interactions; however, this leads to the loss of a considerable body of unique information necessary for solving structural-chemical problems.

Quantum-chemical calculations of anisotropic hyperfine coupling (AHFC) tensors[4,6] can to a great extent facilitate the analysis and interpretation of the solid-state ESR spectra of free radicals complicated by anisotropy. Moreover, such calculations make it possible to relate experimental data to peculiarities of electronic structure of the objects under study. However, the problem of quantitative description of the AHFC constants is more complex and labor-consuming. For this reason, only a few studies concerning consistent calculations of the AHFC constants have been reported, in contrast to a wealth of theoretical data on the isotropic hyperfine coupling (IHFC) constants.

Currently, systematic quantum-chemical calculations of the AHFC tensors for several simple free radicals have been performed (see Ref. 6) in the framework of either essentially simplified semiempirical CNDO and INDO approximations or a specially adapted *ab initio* computational scheme using a carefully chosen basis set of Gaussian functions (9s, 5p),[7] which makes it possible to calculate the spin density on a nucleus with a reasonable accuracy. However, even in the case of not too complex radical systems such an approach becomes inapplicable because of computational problems. At the same time, widely used simplified *ab initio* methods[8] (of the UHF/6-31G type) cannot satisfactorily describe all interactions between the magnetic moments of an unpaired electron and nuclei (because of inadequacy of the basis set), since often the spin properties are determined by a very fine equilibrium between various structural and electronic effects. Therefore it is not surprising that the magnetic resonance parameters of free radicals (especially, the IHFC constants) obtained from *ab initio* calculations are strongly dependent both on peculiarities of the radical geometry and on the choice of the basis set functions used for calculating the Coulomb and exchange potentials, to say nothing of the convergence of the results upon extending the basis set. Unfortunately, the computational cost of improved *ab initio* calculations which go beyond the Hartree—Fock approximation is too high for such calculations to be used in systematic studies of complex paramagnetic systems.

In this connection other quantum-chemical approaches for assessing the ESR spectral parameters of free radicals deserve particular attention. Recently, interest in nonempirical calculations of IHFC and AHFC parameters was rekindled in connection with the development of an

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alternative line of quantum-chemical investigations, based on density functional theory (DFT). Test calculations (mostly, of the IHFC constants in organic π-electron radicals) using different DFT versions were performed[3] in very large basis sets, which undoubtedly are too large to be used for routine calculations. For this reason, simplified basis sets based on the above-mentioned (9s, 5p) basis set[7] were constructed to be acceptable for calculating complex paramagnetic systems from the computational point of view. The results of test DFT calculations[3] showed that, using a special hybrid B3LYP functional in combination with a relatively small and carefully chosen basis set, it is possible to provide quantitative prediction of IHFC constants in not too complex organic free radicals. However, it should be noted that the components of the AHFC tensors were calculated only occasionally because the corresponding computational procedure is more labor-consuming.

It is obvious that the use of relatively simple but more rigorous approximations of the NDDO type[6] makes the semiempirical approach much easier to improve. For instance, it was shown[9,10] that MNDO calculations reproduce the constants of IHFC with protons $a^{\mathrm{H}}{}_{\mathrm{iso}}$ and some other magnetic nuclei (A) in free radicals fairly well. Therefore it is reasonable to expect that the components of the AHFC tensor ($T_{qq'}{}^{\mathrm{A}}$; q, $q' = x, y, z$), which depend on the spin density $\rho(\boldsymbol{r})$ in the same way as $a^{\mathrm{H}}{}_{\mathrm{iso}}$, also will be satisfactorily reproduced using the MNDO approximation.

Computational procedure

The AHFC tensor describes the dipole-dipole interaction between the magnetic moments of electrons and nuclei. The energy of this interaction depends on the mutual orientation of the electron ($\boldsymbol{S}$) and nuclear ($\boldsymbol{I}$) spins. For free radicals, the Hamiltonian of the interaction has the form[6]

$$\hat{\boldsymbol{H}}_{\mathrm{d}} = \sum_{\mathrm{A}} \sum_{qq'} \hat{\boldsymbol{S}}_q T_{qq'}^{\mathrm{A}} \hat{\boldsymbol{I}}_{q'}^{\mathrm{A}} . \qquad (1)$$

The constants $T_{qq'}{}^{\mathrm{A}}$ (parameters of the spin Hamiltonian) are expressed using fundamental physical constants and the spin density:

$$T_{qq'}^{\mathrm{A}} = g_{\mathrm{e}}\beta_{\mathrm{e}}\gamma_{\mathrm{A}}\hbar \int \rho(\boldsymbol{r})\hat{\tau}_{qq'}^{\mathrm{A}}\mathrm{d}\boldsymbol{r}, \qquad (2)$$

where g_{e} is the g-factor of free electron, β_{e} is the Bohr magneton, γ_{A} is the gyromagnetic ratio for nucleus A, $\hbar = h/(2\pi)$, h is the Planck constant, and $\hat{\tau}_{qq'}{}^{\mathrm{A}}$ are the components of the operator of dipole-dipole interaction between the electron and the magnetic nucleus A. In the MO LCAO approximation, the spin density is represented using the spin population matrix ($\rho_{\mu\nu}$) and corresponding atomic orbitals ($\varphi_\mu(\mathbf{r})$, $\varphi_\nu(\mathbf{r})$):

$$\rho(\boldsymbol{r}) = \sum_{\mu,\nu} \rho_{\mu\nu}\varphi_\mu(\boldsymbol{r})\varphi_\nu(\boldsymbol{r}) . \qquad (3)$$

From formulas (2) and (3) it follows that calculations of the AHFC constants require knowledge of the spin populations $\rho_{\mu\nu}$ and the dipole-dipole interaction integrals:

$$\int \varphi_\mu\varphi_\nu\hat{\tau}_{qq'}^{\mathrm{A}}\mathrm{d}\boldsymbol{r} \equiv \left\langle \varphi_\mu\varphi_\nu \middle| \hat{\tau}_{qq'}^{\mathrm{A}} \right\rangle . \qquad (4)$$

Atomic integrals calculated using the Hartree—Fock wave functions have been tabulated.[1,2,5,6] Usually, these integrals are used to assess the spin populations of valence p-AOs from experimental data on anisotropic hyperfine splitting in ESR spectra. Unlike atomic integrals, two-center dipole integrals are less sensitive to the AO type. A procedure is recommended for calculating such integrals with real Slater-type functions with arbitrary effective exponents simulating s- and p-AOs.[6] The integrals are represented analytically *via* auxiliary functions widely used in quantum-chemical calculations.

The obtained AHFC tensor can always be diagonalized by passing to the system of its principal axes. As a rule, the AHFC tensor is diagonal in the system of its principal local symmetry axes, which is a consequence of directionality of chemical bonds. It should be noted that the AHFC tensor defined using formula (2) has a zero spur.

Thus, to perform a theoretical interpretation of experimental values of magnetic resonance parameters of a free radical (in particular, components of the AHFC tensor), one should carry out standard quantum-chemical calculations of the system and find the spin density distribution according to formula (3) and unknown magnetic interaction integrals defined by expression (4). To this end, the above-mentioned general algorithm of calculations of the AHFC constants was implemented using the widely accepted semiempirical MNDO approximation.[11] In this case no essential corrections were introduced into the specially developed computational procedure evaluated earlier.[12]

Results and Discussion

Using the computational procedure outlined above, we calculated the principal values of the AHFC tensors for the representative set of 17 well-studied simplest free radicals (Table 1). Recently,[10] this set of radicals was used as the test set in evaluating a new procedure for quantum-chemical estimates of constants of IHFC with protons in the framework of the semiempirical MNDO approach.

According to calculations,[6,9,10] the constants of IHFC with magnetic nuclei in free radicals, obtained from the MNDO calculations, are in fairly good agreement with experimental data if the assumed structural parameters of radicals are close to real ones. Analogous agreement between theoretical and experimental values should also be expected when performing quantum-chemical analysis of anisotropic characteristics of radicals. Unfortunately, the MNDO/UHF optimization of geometric parameters of paramagnetic systems often leads to unsatisfactory results.[9,10] Because of this, it is appropriate to assess the components of the AHFC tensors in the MNDO approximation using the "reliable" radical geometry determined either experimentally or by more precise computational methods, as in the case of IHFC constants.

The geometric parameters of the free radicals constituting the test set are shown in Table 1. The experimental values and the values found from *ab initio* calculations with the 6-31G** basis set (if no experimental geometries were available) were taken as "reliable" (type of geometry I). Listed also are the structural parameters obtained from MNDO/UHF optimization (type of geometry II). As can be seen from the data listed in Table 1, for many radicals the differences between the "reliable" bond lengths and bond angles and those calculated in the MNDO approximation do not exceed 0.05 Å and 5°, respectively. Nevertheless, even so small differences can strongly affect quantum-chemical estimates of magnetic resonance parameters.[6] At the same time, for radicals **8—10**, **13**, and **17** the differences between the two types of geometric parameters (I and II, see Table 1) are larger, which can lead not only to quantitatively, but also to qualitatively incorrect predictions of the principal values of the AHFC tensors.

Using the two above-mentioned types of geometry, we performed MNDO calculations of the AHFC constants for each of the 17 test free radicals. For all of them, Table 2 lists the principal values of the AHFC tensors, obtained in the framework of the MNDO/RHF approach for the "reliable" geometry and by the MNDO/UHF method for both geometry types (I and II, see Table 1). As can be seen, for most of the radicals the AHFC constants calculated using the geometry types I and II are very close (for **2** and **6** they coincide). As should be expected, particularly large absolute deviations (from ~4 to ~14 Oe) are observed for radicals **8**, **9**, and **13** because the largest differences in the geometric parameters are obtained (see Table 1). However, the same reason is also responsible for much smaller abso-

Table 1. Bond lengths (*d*) and bond angles (ω) in free radicals with different types of geometry (I or II)

Radical	Symmetry	Bond	d/Å		Angle	ω/deg	
			I	II		I	II
$CH_2^{-\cdot}$ (**1**)	C_{2v}	C—H	1.121	1.107	H—C—H	104.4	107.0
$CH_3^{\cdot}$ (**2**)	D_{3h}	C—H	1.079	1.078	H—C—H	120.0	120.0
$NH_2^{\cdot}$ (**3**)	C_{2v}	N—H	1.024	1.002	H—N—H	103.0	104.5
$NH_3^{+\cdot}$ (**4**)	D_{3h}	N—H	1.020	1.010	H—N—H	120.0	120.0
$CN^{\cdot}$ (**5**)	$C_{\infty v}$	C—N	1.172	1.155			
$N_2^{+\cdot}$ (**6**)	$D_{\infty h}$	N—N	1.116	1.094			
$H_2O^{+\cdot}$ (**7**)	C_{2v}	O—H	0.999	0.969	H—O—H	112.6	112.6
$HCO^{\cdot}$ (**8**)	C_s	C—H	1.125	1.074			
		C—O	1.175	1.185	H—C—O	125.0	143.1
$HO_2^{\cdot}$ (**9**)	C_s	O—H	0.958	0.976	H—O—O	105.0	112.4
		O—O	1.300	1.208			
$CO_2^{-\cdot}$ (**10**)	C_{2v}	C—O	1.250	1.235	O—C—O	130.0	137.0
$NO_2^{\cdot}$ (**11**)	C_{2v}	N—O	1.197	1.174	O—N—O	134.0	133.1
$HBO^{-\cdot}$ (**12**)	C_s	B—O	1.266	1.221	H—B—O	128.2	131.6
		B—H	1.272	1.231			
$C_2H_3^{\cdot}$ (**13**)	C_s	C—H_α	1.083	1.049	C—C—H_α	130.8	171.7
		C—H_{cis}	1.085	1.092	C—C—H_{cis}	122.3	123.1
		C—H_{trans}	1.083	1.091	C—C—H_{trans}	121.4	122.7
		C—C	1.357	1.308			
$H_2CN^{\cdot}$ (**14**)	C_{2v}	H—C	1.140	1.099	H—C—N	118.5	123.1
		C—N	1.250	1.266			
$H_2CO^{+\cdot}$ (**15**)	C_{2v}	H—C	1.117	1.122	H—C—O	118.5	122.4
		C—O	1.198	1.228			
$O_3^{-\cdot}$ (**16**)	C_{2v}	O—O	1.280	1.228	O—O—O	120.0	116.0
$H_2NO^{\cdot}$ (**17**)	C_s	N—O	1.300	1.225	H—N—O	118.9	117.9
		N—H	0.988	1.023			

Note. Type I denotes "reliable" geometry (geometric parameters of radicals **1**, **10**, and **12—17** were found from *ab initio* calculations in 6-31G** type basis sets and those of radicals **2—9** and **11** were determined experimentally) and type II denotes geometry optimized by the MNDO/UHF method.

lute deviations in radicals **10** and **17**. By and large, noteworthy is that some uncertainties in the geometry of radicals are less significant when calculating the AHFC constants compared to the IHFC constants.[6,9,10]

Differences between the corresponding values obtained from MNDO/UHF and MNDO/RHF calculations are due to the spin polarization effects.[6] Comparison of the components of the AHFC tensors calculated using the two methods for the "reliable" geometry (see Table 2) shows that for most of the radicals studied these effects are insignificant. At the same time, rather large differences between corresponding AHFC parameters

Table 2. Principal values of the AHFC tensors (T/Oe) in free radicals, calculated by the MNDO/RHF and MNDO/UHF methods for different types of geometry (I and II)

Radical	Nucleus	MNDO/RHF,			MNDO/UHF					
		I			I			II		
		T_{11}	T_{22}	T_{33}	T_{11}	T_{22}	T_{33}	T_{11}	T_{22}	T_{33}
1	H	−14.3	−4.3	18.6	−15.6	−6.4	22.0	−16.0	−6.3	22.3
	C	−32.7	−32.7	65.4	−34.4	−29.0	63.4	−34.4	−29.1	63.5
2	H	−15.6	−4.0	19.6	−17.5	−7.9	25.4	−17.5	−7.9	25.4
	C	−32.7	−32.7	65.4	−30.2	−30.2	60.4	−30.2	−30.2	60.4
3	H	−20.4	−9.4	29.8	−22.4	−12.4	34.8	−23.6	−12.4	36.0
	N	−17.2	−17.2	34.4	−17.5	−15.8	33.3	−17.6	−15.8	33.4
4	H	−9.4	−20.6	30.0	−13.8	−23.2	37.0	−13.9	−23.7	37.6
	N	−17.2	−17.2	34.4	−16.3	−16.3	32.6	−16.3	−16.3	32.6
5	C	−17.3	−17.3	34.6	−13.2	−13.2	26.4	−13.7	−13.7	27.4
	N	−5.9	−5.9	11.8	−7.4	−7.4	14.8	−7.1	−7.1	14.2
6	N	−7.2	−7.2	14.4	−7.7	−7.7	15.4	−7.7	−7.7	15.4
7	H	−23.6	−14.3	37.9	−25.7	−17.0	42.7	−27.7	−17.7	45.4
	O	51.8	51.8	−103.6	52.3	48.7	−101.0	52.5	48.7	−101.2
8	H	−6.7	−3.1	9.8	−6.3	−3.0	9.3	−9.3	−4.5	13.8
	C	−12.3	−12.6	24.9	−10.7	−15.2	25.9	−14.4	−17.7	32.1
	O	14.7	13.3	−28.0	17.4	12.6	−30.0	18.4	11.9	−30.3
9	H	−7.4	−7.2	14.6	−5.9	−5.5	11.4	−7.8	−7.1	14.9
	O	16.1	13.0	−29.1	10.1	8.0	−18.1	14.4	11.7	−26.1
	O_t*	37.2	36.0	−73.2	43.7	40.7	−84.4	38.7	37.3	−76.0
10	C	−8.4	−13.6	22.0	−11.1	−12.2	23.3	−11.7	−13.2	24.9
	O	13.7	12.6	−26.3	15.3	14.1	−29.4	14.4	13.4	−27.8
11	N	−2.3	−4.6	6.9	−3.7	−4.2	7.9	−3.5	−4.2	7.7
	O	18.3	17.3	−35.6	22.3	18.8	−41.1	21.7	18.7	−40.4
12	H	−3.4	−3.8	7.2	−2.5	−3.4	5.9	−3.0	−4.0	7.0
	B	−2.7	−4.0	6.7	−0.5	−7.1	7.6	−0.6	−6.8	7.4
	O	11.4	11.6	−23.0	12.7	13.3	−26.0	12.0	13.0	−25.0
13	H_α	−13.6	−3.7	17.3	−15.2	−15.0	30.2	−18.2	−12.2	30.4
	H_{cis}	−2.4	−2.1	4.5	−13.3	1.3	12.0	−11.0	1.0	10.0
	H_{trans}	−2.6	−2.1	4.7	−12.8	1.6	11.2	−10.9	1.1	9.8
	C_α	−29.2	−28.9	58.1	−41.8	9.1	32.7	−42.7	−3.8	46.5
	C_β	−1.5	−1.1	2.6	−34.6	13.1	21.5	−25.4	8.8	16.6
14	H	−2.8	−1.8	4.6	−7.3	0.6	6.7	−7.5	0.9	6.6
	C	−2.3	−0.6	2.9	−12.0	0.3	11.7	−13.8	1.1	12.7
	N	−13.3	−13.1	26.4	−18.9	−7.7	26.6	−19.5	−7.0	26.5
15	H	−3.8	−2.6	6.4	−4.6−	−0.5	5.1	−4.3	0.0	4.3
	C	−2.0	0.1	1.9	3.8	−1.7	5.5	−4.0	−1.9	5.9
	O	31.4	31.3	−62.7	43.4	32.7	−76.1	44.7	33.1	−77.8
16	O_c**	19.9	18.5	−38.4	23.4	20.7	−44.1	23.4	20.6	−44.0
	O_t*	16.8	14.9	−31.7	15.1	14.0	−29.1	15.3	13.8	−29.1
17	H	−10.0	−5.9	15.9	−9.2	−6.7	15.9	−7.8	−5.0	12.8
	N	−7.9	−6.6	14.5	−6.0	−5.1	11.1	−5.0	−3.9	8.9
	O	30.0	28.3	−58.3	33.8	33.7	−67.5	32.4	32.2	−64.6

Note. For notations "I" and "II," see note to Table 1.

* Terminal atom.

** Central atom.

Table 3. Principal values of the AHFC tensors (T/Oe) in free radicals,[6] obtained experimentally and from INDO and *ab initio* calculations

Radical	Nucleus	Experiment			Calculations					
		T_{11}	T_{22}	T_{33}	INDO			*Ab initio*		
					T_{11}	T_{22}	T_{33}	T_{11}	T_{22}	T_{33}
4	H	−2.1	−19.6	21.7	−7.5	−22.0	29.5	—	—	—
5	C	−16.0	−16.0	32.0	−12.9	−12.9	25.8	−8.6	−8.6	17.2
	N	−5.5	−5.5	11.0	−5.0	−5.0	10.0	−4.8	−4.8	9.6
8	H	−6.1	−2.9	9.0	−6.1	−2.5	8.6	−6.4	−4.8	11.2
	C	−8.6	−17.3	25.9	−10.8	−6.1	16.9	−10.8	−22.2	33.0
10	C	−11.7	−16.7	28.4	−11.8	−4.0	15.8	−10.4	−7.6	18.0
	O	10.1	8.9	−19.0	10.0	9.4	−19.4	—	—	—
11	N	−5.4	−7.8	13.2	−5.0	−2.9	7.9	−5.0	−3.8	8.8
	O	21.1	16.9	−38.0	13.0	11.5	−24.5	14.8	13.5	−28.3
12	H	−4.0	−4.0	8.0	−6.6	−5.0	11.6	−4.7	−1.7	6.4
	B	−6.0	−6.0	12.0	−7.8	−5.8	13.6	−8.4	−10.9	19.3
14	N	−12.5	−12.5	25.0	−12.5	−14.3	26.8	−12.5	−17.7	30.2

for radical **13** should be pointed out. It is noteworthy that the spin polarization effects also were of particular importance in performing quantum-chemical estimates of the IHFC constants for the vinyl σ-radical.[10]

The experimentally found principal values of the tensors of AHFC with several nuclei for a number of radicals constituting the test set, as well as corresponding values calculated either in the INDO approximation or in the framework of the above-mentioned *ab initio*[6] approach, are listed in Table 3. Comparison of the data listed in Tables 2 and 3 shows that the experimental T_{22}^{H} component for the $NH_3^{+\cdot}$ (**4**) radical is fairly well reproduced in the MNDO approximation, whereas the $|T_{11}^{H}|$ and $|T_{33}^{H}|$ values are overestimated by 10—15 Oe. The fact that the $CN^{\cdot}$ radical (**5**) has a cylindrical symmetry is reflected in the magnitudes of all principal T_{11} and T_{22} values for both tensors of AHFC with the ^{13}C and ^{14}N nuclei; the values obtained from MNDO/RHF calculations (see Table 2) and experimental ones (see Table 3) are particularly close. For the $HCO^{\cdot}$ radical (**8**), all AHFC constants assessed by the MNDO/UHF method are in good agreement with experimental values; however, this is observed only for the "reliable" (type I) rather than for optimized (type II) geometry.

From comparison of the data listed in Tables 2 and 3 it can be seen that the principal values of the tensors of AHFC with the ^{13}C nuclei for the σ-electron $CN^{\cdot}$, $HCO^{\cdot}$, and $CO_2^{-\cdot}$ radicals, calculated in the MNDO approximation, are much closer to experimental values than corresponding values obtained from *ab initio* calculations. The same is also observed for the ^{17}O nucleus in the $NO_2^{\cdot}$ σ-radical (**11**), which is isoelectronic to the $CO_2^{-\cdot}$ radical. For the $HBO^{-\cdot}$ (**12**) and $H_2CN^{\cdot}$ (**14**) radicals, the components of the AHFC tensors, calculated in the framework of both the *ab initio* and MNDO computational schemes differ from experimental values nearly to the same extent.

When analyzing the differences between theoretical and experimental AHFC parameters it should be kept in mind that the matrix stabilizing free radicals is to some extent capable of affecting them. Quantum-chemical calculations of magnetic resonance parameters of free-radical systems are usually carried out ignoring this effect because its correct consideration is very difficult. Additionally, in those cases where the electron correlation effects are particularly strong, drawbacks of the Hartree—Fock approximation can strongly affect the results of calculations.

By and large, it can be said that the MNDO and INDO approximations are characterized by nearly equal efficiency in performing quantum-chemical estimates of the AHFC constants for the chosen test set of radicals, though in some instances (*e.g.*, radicals **8**, **10**, and **11**) the simplified semiempirical INDO version is less appropriate. At the same time, it should be noted that some of the results of *ab initio* and semiempirical (MNDO/UHF) calculations of the AHFC parameters in the radicals considered proved to be appreciably different. In these cases the components of the AHFC tensors, assessed in the framework of the MNDO scheme, appeared to be much closer to experimental values than those calculated using the *ab initio* approach (see Tables 2 and 3). Thus, the MNDO computational procedure is appropriate for semiquantitative description of the AHFC constants in free radicals and its success is at least on a par with the INDO and *ab initio* approximations used previously.[6,12] In this connection, non-empirical quantum-chemical calculations of the AHFC tensors of complex free-radical systems using DFT methods seem to be the most promising, since recent evaluations[3,13—18] of these methods demonstrate that they are highly efficient.

References

1. 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.
2. A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance with Application to Chemistry and Chemical Physics*, Harper and Row Publishers, New York—Evanston—London, 1967.
3. C. Adamo, V. Barone, and A. Fortunelli, *J. Chem. Phys.*, 1995, **102**, 384.
4. P. V. Schastnev, *Teoriya elektronnykh obolochek molekul. Ch. III. Elektricheskie i magnitnye svoistva* [*Theory of Molecular Electron Shells. Pt. III. Electric and Magnetic Properties*], Izd. Novosibirskogo Gos. Univ., Novosibirsk, 1978, 88 pp. (in Russian).
5. Yu. V. Rakitin, G. M. Larin, and V. V. Minin, in *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* [*Interpretation of ESR Spectra of Coordination Compounds*], Nauka, Moscow, 1993, p. 399 (in Russian).
6. 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).
7. S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 293.
8. W. J. Hehre, L. Radom, P. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley Interscience, New York, 1986.
9. 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 [*Moscow Univ. Bull., Ser. 2, Chem.*, 1992 (Engl. Transl.)].
10. N. D. Chuvylkin and A. M. Tokmachev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1459 [*Russ. Chem. Bull*, 1999, **48**, 1442 (Engl. Transl.)].
11. T. Clark, *A Handbook of Computational Chemistry*, J. Wiley and Sons, New York, 1985.
12. N. D. Chuvylkin and G. M. Zhidomirov, *J. Magn. Res.*, 1973, **11**, 367.
13. L. A. Ericsson, V. G. Malkin, O. L. Malkina, and D. R. Salahub, *Int. J. Quantum Chem.*, 1994, **52**, 879.
14. J. M. Martell, R. J. Boyd, and L. A. Ericsson, *J. Phys. Chem.*, 1995, **99**, 623.
15. P. J. O'Malley and D. A. Ellson, *Chem. Phys. Lett.*, 1996, **260**, 492.
16. P. J. O'Malley and D. A. Ellson, *Biochim. Biophys. Acta*, 1997, **1320**, 65.
17. P. J. O'Malley, *Chem. Phys. Lett.*, 1996, **262**, 797.
18. M. T. Nguyen, S. Creve, L. A. Ericsson, and L. G. Vanquickenborne, *Mol. Phys.*, 1997, **91**, 537.

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