Evaluation of MNDO approximation in quantum-chemical calculations of *g*-tensors of 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

The MNDO approximation was tested for applicability in calculations of the *g*-tensors of free radicals. The representative test set included 15 free radicals for which the isotropic and anisotropic hyperfine coupling constants were calculated previously in the framework of the MNDO approach.

Key words: ESR spectroscopy, free radicals, *g*-tensors, quantum-chemical calculations, MNDO approximation.

Modern radiospectroscopic methods make it possible to record a complete set of magnetic resonance parameters of free-radical systems with spin $s = 1/2$, *i.e.*, the *g*-factor and the isotropic and anisotropic hyperfine coupling constants (IHFC and AHFC, respectively). These characteristics obtained from ESR spectra can then be used for determination of structural parameters of these systems. Often, it is helpful (and even necessary) to analyze radiospectroscopic information on the paramagnetic compound under study using quantum-chemical methods.[1–4]

Reliable assignment of an experimental ESR spectrum to a particular structure of free radical with $s = 1/2$ requires quantum-chemical calculations of all magnetic resonance parameters of the radical, *i.e.*, the complete set of the IHFC and AHFC constants as well as the components of the *g*-tensor. Previously,[3,5] we have tested the MNDO approximation for applicability in systematic quantum-chemical estimates of the IHFC constants and AHFC tensors taking several experimentally and theoretically well-studied test free radicals as examples. However, the *g*-factor is not the less important spectroscopic characteristic. Moreover, in the absence of magnetic nuclei in a free radical, the *g*-factor is the only magnetic resonance parameter that can be determined by ESR spectroscopy. Therefore, this work is dedicated to an analogous evaluation of the MNDO approximation in quantum-chemical calculations of *g*-tensors of the test free radicals.

Calculation procedure

Neglecting nuclear spins, the spin Hamiltonian of a radical system with $s = 1/2$ can be written in the form[1]

$$\hat{H}_s = \beta_e H g \hat{S}, \tag{1}$$

where β_e is the Bohr magneton, H is the magnetic field strength, g is the *g*-tensor, and $\hat{S}$ is the electron spin operator.

This spin Hamiltonian determines the Zeeman energy of an electron and makes it possible to relate the Zeeman splitting in the ESR spectrum to the spatial orientation of the free-radical particle. The deviations of the diagonal components of the *g*-tensor from the *g*-factor of free electrons ($g_e = 2.0023$) are due to spin-orbital coupling

$$\hat{H}_{sl} = \xi(r)\hat{l}\cdot\hat{S}. \tag{2}$$

This interaction is due to obital motion of the unpaired electron. Polyatomic systems are usually considered using the following approximation[1] for $\hat{H}_{sl}$:

$$\hat{H}_{sl} = \sum_K \xi_K(r_K)\hat{l}_K\cdot\hat{S}, \tag{3}$$

where $\xi_K(r_K)$ is the spin-orbital coupling constant of the *K*th atom and $\hat{l}_K$ is the orbital angular momentum operator of the electron with respect to the nucleus of the *K*th atom.

Only a few rigorous quantum-chemical calculations of the *g*-tensors based on expression (3) were reported to date.[6–8] This is due to the fact that calculations of the *g*-factor in the framework of perturbation theory requires summation of contributions from many excited states. Therefore, *ab initio* calculations of *g*-tensors can be carried out only for rather small systems even in the minimum basis sets.

In this connection other quantum-chemical approaches to assessing the ESR spectral parameters of free radicals deserve particular attention. Currently, interest in consistent calculations of *g*-tensors[8,9] is rekindled in connection with the development of an alternative line of quantum-chemical investigations, based on the density functional theory (DFT).[10]

At the same time, systematic quantum-chemical estimates of the components of *g*-tensors, especially in the case of relatively complex paramagnetic compounds, are still carried out using well-approved semiempirical methods.[1] In this case,

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 601—604, April, 2000.

it should be kept in mind that the development of a rather simple and reliable computational procedure for extracting structural-chemical information from the ESR spectra is difficult because of the lack of reliable experimental data on the g-tensors of small free-radical systems. Most of these systems were studied in the liquid phase, characterized by chaotic motion of radicals, which results in averaging. As a result, only the isotropic value $g_{\rm iso} = (g_{11} + g_{22} + g_{33})/3$ can be measured, which usually differs slightly from the g_e-factor of the free electron.

In the framework of the semiempirical approach, it is accepted to use the approximate Stone formula[1] obtained in the one-determinant representation of the ground and n excited states of a paramagnetic system (with energies E_0 and E_n, respectively). For a nondegenerate doublet configuration of the radical containing only the atoms with s- and p-valence atomic orbitals (AOs) φ_μ, this formula has the form

$$g_{qq'} = g_e + \Delta g_{qq'}, \tag{4}$$

$$\Delta g_{qq'} = -2\sum_n \sum_K \sum_P \frac{\xi_P \cdot \langle \Psi_0 | \hat{l}_{Kq} | \Psi_n \rangle \langle \Psi_n | \hat{l}_{Pq'} | \Psi_0 \rangle}{E_n - E_0}, \tag{5}$$

where q and q' are the axes of coordinates, Ψ_0 is the molecular orbital (MO) of the unpaired electron, Ψ_n is any other MO, and ξ_P is the spin-orbital coupling constant

$$\xi_P = \int \varphi_P \xi_P(r) \varphi_P {\rm d}r. \tag{6}$$

Summation in expression (5) is performed over all atoms K and P. The matrix element of the $\hat{l}_{Pq}$ operator is assumed to be equal to zero if it acts on the φ_μ AO, which does not belong to the Pth atom.

Previously,[11] a simplified procedure based on the λ-variant of the CNDO/SP scheme and the approximate Stone formula was proposed for calculations of the g-factor. It uses the differences of the orbital energies $(\varepsilon_n - \varepsilon_0)$ instead of the energies of electron excitations $(\Delta E = E_n - E_0)$ and the error due to this assumption is compensated by the empirical parameter λ_g used in the formula

$$g = g_e I + \lambda_g \Delta g. \tag{7}$$

Quantum-chemical calculations in the CNDO/SP approximation have shown that satisfactory agreement with experimental data is obtained using a λ_g value of 4 and Hartree—Fock values of the spin-orbital coupling constants ξ_P in expression (5), calculated using formula (6) for neutral atoms.[11,12]

An improved approach (γξ-variant) developed more recently[1] correctly uses calculated energies of electron excitations in expression (5) and takes into account the dependence of the spin-orbital coupling constants on the excess atomic charges in the radical. The excitation energies are calculated using the known relationships:

$$E_v - E_0 = \varepsilon_v - \varepsilon_0 - J_{v0} + 0.5J_{00} + 0.5K_{v0} \tag{8}$$

and

$$E_{\rm d} - E_0 = \varepsilon_{\rm d} - \varepsilon_0 + J_{\rm d0} - 0.5J_{00} - 0.5K_{\rm d0}, \tag{9}$$

where ε_v and $\varepsilon_{\rm d}$ are the energies of virtual (Ψ_v) and doubly occupied $(\Psi_{\rm d})$ MOs, ε_0 is the MO energy of the unpaired electron, and J_{n0} and K_{n0} are the Coulomb and exchange integrals, respectively. Both approaches result in qualitatively coinciding results, though for several radicals ($NO_2^{\bullet}$, $CO_2^{\bullet-}$, $HCO^{\bullet}$, $CH_3CO^{\bullet}$) the improved γξ-scheme gives a somewhat better quantitative agreement with experiment than the λ-variant.[1] By and large, the simplified λ-procedure makes it possible to semiquantitatively reproduce experimentally observed trends in changes in the magnitudes of the components of g-tensors of the representative set of free radicals.

Taking into account all outlined above, in this work we implemented the λ-algorithm of calculations of the g-tensors of free radicals in the framework of the Stone approach using the widely accepted semiempirical MNDO approximation.[13] As in the case of the AHFC tensors,[5] the specially developed and evaluated[11] computational procedure for calculations of g-tensors also did not undergo essential changes. A satisfactory agreement between theoretical and experimental values of the components of g-tensors in this case is obtained at $\lambda_g = 8$.

Results and Discussion

The principal values of the g-tensors calculated in the MNDO approximation as well as the corresponding isotropic $g_{\rm iso}$ values for 15 test free radicals are listed in Table 1. Analogous data obtained experimentally and calculated using the λ-variant of the CNDO/SP[1] approach are also presented here for comparison. Calculations were carried out for the same "reliable" structures used previously[3,5] in obtaining systematic quantum-chemical estimates of the IHFC constants and AHFC tensors of these radicals. Only the $g_{\rm iso}$ values were experimentally determined for $C_2H_3^{\bullet}$, $H_2CN^{\bullet}$, $NH_2^{\bullet}$, and $BH_3^{\bullet-}$ radicals, whereas the components of the g-tensor were not measured because of their averaging.

For σ-electron radicals $C_2H_3^{\bullet}$ and $H_2CN^{\bullet}$, the $g_{\rm iso}$ values calculated in the MNDO approximation coincide with the experimental data (see Table 1). The differences between the $g_{\rm iso}$ values and the g_e-factor of the free electron obtained by the CNDO/SP method somewhat differ from those observed experimentally, though they correctly reflect the qualitative picture. The theoretical $g_{\rm iso}$, g_{11}, and g_{22} values obtained for σ-radical $CN^{\bullet}$ are close to the corresponding experimental values. However, both approaches do not reproduce a decrease in the g_{33} value compared to g_e. On the whole, the MNDO (λ_g) variant gives much better agreement with experiment than CNDO/SP (λ_g) variant for this radical.

The data listed in Table 1 indicate that the MNDO approximation is also much more efficient than the CNDO/SP scheme for structurally similar σ-electron radicals $HCO^{\bullet}$ and $CH_3CO^{\bullet}$, especially for evaluation of the g_{11} values of their g-tensors. Substantially smaller absolute deviations of the g_{11} principal values from the corresponding experimental values were also obtained by the MNDO (λ_g) method for isoelectronic paramagnetic particles $CO_2^{\bullet-}$ and $NO_2^{\bullet}$ with the unpaired electron on the σ-MO. On the contrary, the components of the g-tensors of σ-radical $HCN^{\bullet-}$ and π-radicals $NH_2^{\bullet}$, $NH_3^{\bullet+}$, $H_2NO^{\bullet}$, and $O_3^{\bullet-}$, calculated using the CNDO/SP (λ_g)-variant, demonstrate better agreement with experiment than those assessed using the MNDO approach. For the $HCN^{\bullet-}$ radical anion this is most likely due to inaccurate determination of its "reliable" geometry (see Ref. 3) obtained from *ab initio*

Table 1. Experimental[11] and calculated principal values of the **g**-tensors of free radicals

Radical	Experiment				Calculations							
	g_{iso}	g_{11}	g_{22}	g_{33}	MNDO (λ_g)				CNDO/SP (λ_g)			
					g_{iso}	g_{11}	g_{22}	g_{33}	g_{iso}	g_{11}	g_{22}	g_{33}
$C_2H_3^{\cdot}$	2.0022	—	—	—	2.0022	2.0023	2.0022	2.0022	2.0021	2.0024	2.0023	2.0017
$CN^{\cdot}$	2.0008	2.0003	2.0003	2.0015	2.0009	2.0002	2.0002	2.0023	2.0006	1.9998	1.9998	2.0023
$HCN^{\cdot -}$	2.0022	2.0039	2.0022	2.0005	2.0019	2.0034	2.0028	1.9995	2.0020	2.0036	2.0022	2.0001
$H_2CN^{\cdot}$	2.0030	—	—	—	2.0030	2.0044	2.0032	2.0015	2.0027	2.0042	2.0023	2.0017
$HCO^{\cdot}$	2.0003	2.0037	2.0023	1.9948	2.0017	2.0038	2.0024	1.9988	2.0019	2.0055	2.0021	1.9983
$CH_3CO^{\cdot}$	2.0005	2.0038	2.0022	1.9960	1.9997	2.0039	2.0023	1.9927	2.0021	2.0061	2.0027	1.9974
$CO_2^{\cdot -}$	2.0007	2.0032	2.0016	1.9973	2.0012	2.0069	2.0024	1.9943	2.0022	2.0085	2.0024	1.9957
$NH_2^{\cdot}$	2.0048	—	—	—	2.0029	2.0023	2.0024	2.0041	2.0036	2.0023	2.0030	2.0055
$NH_3^{\cdot +}$	2.0035	2.0020	2.0040	2.0040	2.0029	2.0023	2.0032	2.0032	2.0035	2.0023	2.0041	2.0041
$H_2NO^{\cdot}$	2.0059	2.0027	2.0061	2.0089	2.0089	2.0024	2.0047	2.0201	2.0076	2.0023	2.0074	2.0132
$NO_2^{\cdot}$	1.9994	2.0061	2.0013	1.9908	2.0010	2.0094	2.0025	1.9911	2.0020	2.0114	2.0023	1.9923
$HBO^{\cdot -}$	2.0020	2.0060	2.0060	1.9970	2.0019	2.0035	2.0023	1.9999	2.0021	2.0048	2.0020	1.9994
$BH_3^{\cdot -}$	2.0015	—	—	—	2.0022	2.0023	2.0022	2.0022	2.0021	2.0023	2.0020	2.0020
$O_3^{\cdot -}$	2.0115	2.0035	2.0123	2.0187	2.0123	2.0023	2.0137	2.0211	2.0118	2.0023	2.0142	2.0189
$H_2CO^{\cdot +}$	2.0036	2.0069	2.0025	2.0015	2.0038	2.0062	2.0037	2.0014	—	—	—	—

Note. Only the deviations of the principal values of **g**-tensors from the pure spin value of the g_e-factor of a free electron can be obtained from calculations.

calculations in the 6-31G** basis set and introduced into the MNDO (λ_g) computational procedure instead of being fitted on the basis of empirical criterion as in the CNDO/SP approach.[1] Noteworthy also is that, as follows from the data obtained by both theoretical methods (see Table 1), the **g**-tensor of the σ-electron radical $HBO^{\cdot -}$ should not have axial symmetry.

For 6 out of 15 test radicals presented in Table 1, the **g**-tensors were calculated in the framework of *ab initio* and DFT approaches (see Ref. 8). The principal values calculated in this work using systematized[8] data of *ab initio* and DFT calculations are presented in Table 2. Comparison of the corresponding values in Tables 1 and 2 shows that at a qualitative level both the nonempirical approach and semiempirical method evaluated in this work reproduce experimental regularities for the six radicals in a similar way. The smallest quantitative discrepancies with the experiment for the principal values of **g**-tensors were achieved by using the DFT approach for isoelectronic σ-radicals $CO_2^{\cdot -}$ and $NO_2^{\cdot}$ and by using the MNDO (λ_g)-variant for dissimilar paramagnetic particles $CN^{\cdot}$ and $H_2CO^{\cdot +}$ with the unpaired electron on the σ-MO. In the case of σ-radical $HCO^{\cdot}$, the g_{11} principal value assessed by the MNDO (λ_g) method is much closer to the experimental value than that calculated using *ab initio* or DFT approaches; however, the reverse is observed for the g_{33} principal value.

On the whole, our calculations of **g**-tensors of the representative set of 15 test radicals show that the MNDO approximation makes it possible to obtain qualitatively correct results reproducing the experimentally found deviations of the g_{qq} principal components from the g_e-factor of a free electron. In some cases, a quantitatively acceptable accuracy can be achieved. The results of MNDO (λ_g) calculations of σ-electron radicals are, as a rule, in better quantitative agreement with the experimental data than those of CNDO/SP (λ_g) calculations. Taking into account the results of previous studies,[1] we can say that an increase in the accuracy of description of radiospectroscopic data on the **g**-tensors of free radicals in the framework of MNDO approximation first of all requires a more correct evaluation of the energies of electron excitations using Eqs. (8) and (9).

Table 2. Principal values of the **g**-tensors of free radicals calculated using systematized[8] data of *ab initio* and DFT calculations*

Radical	*Ab initio*				DFT			
	g_{iso}	g_{11}	g_{22}	g_{33}	g_{iso}	g_{11}	g_{22}	g_{33}
$CN^{\cdot}$	—	2.0015	2.0015	—	2.0006	1.9998	1.9998	2.0022
$HCO^{\cdot}$	2.0011	2.0041	2.0024	1.9968	1.9999	2.0050	2.0020	1.9928
$CO_2^{\cdot -}$	2.0016	2.0041	2.0024	1.9984	2.0001	2.0038	2.0015	1.9951
$NO_2^{\cdot}$	2.0000	2.0058	2.0021	1.9920	1.9988	2.0064	2.0015	1.9886
$O_3^{\cdot -}$	2.0158	2.0023	2.0138	2.0312	2.0121	2.0017	2.0128	2.0217
$H_2CO^{\cdot +}$	2.0065	2.0088	2.0079	2.0027	2.0040	2.0085	2.0024	2.0011

* See note to Table 1.

References

1. 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).
2. I. Yu. Shchapin and N. D. Chuvylkin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 321 [*Russ. Chem. Bull.*, 1996, **45**, 306 (Engl. Transl.)].
3. N. D. Chuvylkin and A. M. Tokmachev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1459 [*Russ. Chem. Bull.*, 1999, **48**, 1442 (Engl. Transl.)].
4. N. D. Chuvylkin and A. M. Tokmachev, *Mendeleev Commun.*, 1999, **9**, 183.
5. N. D. Chuvylkin and A. M. Tokmachev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 2242 [*Russ. Chem. Bull.*, 1999, **48**, 2216 (Engl. Transl.)].
6. G. H. Lushington, P. Bündgen, and F. Grein, *Int. J. Quant. Chem.*, 1995, **55**, 377.
7. G. H. Lushington and F. Grein, *Int. J. Quant. Chem.*, 1996, **60**, 467.
8. G. Schreckenbach and T. Ziegler, *J. Phys. Chem., A*, 1997, **101**, 3388.
9. E. van Lenthe, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.*, 1997, **107**, 2488.
10. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, Oxford, 1989.
11. N. D. Chuvylkin and G. M. Zhidomirov, *Mol. Phys.*, 1973, **25**, 1233.
12. 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.
13. T. Clark, *A Handbook of Computational Chemistry*, J. Wiley and Sons, New York, 1985.

Received June 30, 1999