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Theoretical Study of ^{14}N, ^{17}O, and ^{19}F Hyperfine Coupling Constants

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The ^{1}H hyperfine coupling constants of free radicals and ions have been successfully studied by our newly modified s-p separation type INDO-MO method[1-4], and the most of our calculated coupling constants are significantly better than the corresponding results of the conventional INDO-MO method.[5,6]

The nuclear hyperfine coupling constant is assumed to be directly proportional to the 2s spin density for the cases of elements nitrogen, oxygen and fluorine. Linear correlation study between spin densities and the isotropic hyperfine coupling constants of ^{14}N, ^{17}O and ^{19}F have been carried out for the related free radicals and ions. In the ^{17}O and ^{19}F cases, both our results are better than the corresponding results of the conventional INDO-MO method.[6] The statistical results of ^{14}N case are quite similar to the corresponding results of Pople et al.[6]

I. INTRODUCTION

Since the s-p separation INDO-MO model was introduced by Chen et al.[1], it has been successfully applied to both closed and open shell problems.[1-4,7,8] In order to test the substantial improvement over the conventional INDO-MO method in the cases of open shell calculation, 57 free radical and ions were selected as the example to study their MO and ^{1}H hyperfine coupling constants (a_H) calculations in our former work[2-4]. In that work, 138 various a_H's within 57 radicals were studied with linear correlation type treatment. By comparison of the standard deviations, correlation coefficients and the number of smaller $|(a)_{cal} - (a)_{obs}|$ (or better $(a)_{cal}$) between this method and the conventional INDO method in the least squares type statistical calculation, all the evidence shows that our modified INDO-MO is significantly better than the conventional method.[5-6]

Similar to the former treatment of a_H for ^{1}H, we applied this MO method to the problem of hyperfine coupling constants (a_N) calculation of ^{14}N, ^{17}O and ^{19}F. By this theoretical calculation and interpretation we are going to verify that our newly developed MO method in this work is one of the reliable semiempirical methods for the theoretical study of open shell free radicals and their ESR spectra in general.

II. CALCULATION

In this work, three series of free radicals and ions were chosen for MO calculation. For a_N's of ^{14}N, we selected 26 radical ions with 29 various kinds of ^{14}N including benzonitril anion etc., in the first series. For a_N's of ^{17}O, five radical ions with five different kinds of ^{17}O including p-benzosemiquinone anion etc. were chosen in the second series. In the last series for a_N's of ^{19}F, eight free radicals and ions with nine various kinds of ^{19}F including fluoromethyl radical etc. were selected.

The MO theory and the computer program of this calculation are the same as those used in our earlier works.[1–4,78] Since then we have found that the separation of σ and π bond parameters for 2p orbitals ($\beta^{\sigma}_{2p} \neq \beta^{\pi}_{2p}$) usually gives better MO results than the single β_{2p} type calculation[1–4], as shown in our recent papers[7,8]. The cases of both types of bond parameter were used for comparison. The above mentioned bond parameters of various cases are all listed in Table I. Most of the atomic parameters used here are similar to the parameters that we used in our former works[1,7,8], except that we have chosen orbital exponent of hydrogen $Z_H' = 1.2$, the conventional value[1,5–8], for various cases. By combination of different types of calculation parameters, four sets of calculation have been set up for each of the above mentioned series. We define the MO calculation with $\beta^{\sigma}_{2p} \neq \beta^{\pi}_{2p}$ and $Z_H' = 1.2$ as the first set, the MO calculation with single β_{2p} and $Z_H' = 1.2$ as the second set, the MO calculation with $\beta^{\sigma}_{2p} \neq \beta^{\pi}_{2p}$ and $Z_H' = 1.0$ as the third set, and the

TABLE I

Bond parameters (in e V)

atom	Orbital		$\beta_{2p}{}^{1-4}$ nonseparated	$\beta^{\pi}_{2p} \neq \beta^{\sigma}_{2p}{}^{7-8}$
H	1s	β_{1s}	6.500	6.500
	2s	β_{2s}	23.527	23.527
C	2p	$\beta_{2p}\sigma$ (2p — 2s) $\beta_{2p}\sigma$ (2p — 2p) $\beta_{2p}\pi$ (2p — 2p)	19.061	19.061 30.139 13.732
	2s	β_{2s}	34.051	34.051
N	2p	$\beta_{2p}\sigma$ (2p — 2s) $\beta_{2p}\sigma$ (2p — 2p) $\beta_{2p}\pi$ (2p — 2p)	28.170	28.170 40.164 21.356
	2s	β_{2s}	45.965	45.965
O	2p	$\beta_{2p}\sigma$ (2p — 2s) $\beta_{2p}\sigma$ (2p — 2p) $\beta_{2p}\pi$ (2p — 2p)	38.804	38.804 49.188 27.857
	2s	β_{2s}	60.410	60.410
F	2p	$\beta_{2p}\sigma$ (2p — 2s) $\beta_{2p}\sigma$ (2p —,2p) $\beta_{2p}\pi$ (2p —,2p)	51.347	51.347 49.232 55.300

MO calculation with single β_{2p} and $Z_H' = 1.0$ as the last set. As for the input data of geometrical coordinates of each atom in a molecule, we have calculated them with the standard bond distances and bond angles for free radicals as those proposed by Pople et al.[6]. These standard geometrical parameters are listed in Table II.

TABLE II

Standard bond length (in A°)[6]

	H	C	N	O	F
H	0.78	1.08	1.00	0.96	0.92
C	1.08	1.40	1.37	1.36	1.35
N	1.00	1.37	1.35	1.30	1.36
O	0.96	1.36	1.30	1.48	1.42
F	0.92	1.35	1.36	1.42	1.42

The SCF procedure used here is the same as that used in our former works,[1-8] the iterative calculation is regarded to be self-consistent whenever the relative error of total electronic energy is less than 10^{-6}. All MO calculations attained their self-consistency successfully within the 29th iterations. The MO calculation completed, we picked up the spin densities of 2s orbitals of the related atoms and then preformed our linear least squares analysis by using Eq. (1) and the related observed hyperfine coupling constants from References[9-26] to calculate a_N's for various series of free radicals and ions.

$$a_N = K \varrho_N \tag{1}$$

$$K = K \mid \Phi_{2s}(R) \mid^2 \tag{2}$$

$$K_N = \frac{2}{3} \, g \, \beta \, \gamma_N \, h \, \langle \hat{S}_z \rangle^{-1} \tag{3}$$

In Eq. (1) a_N and ρ_N are the spin density and hyperfine coupling constants of the related nucleus N. For the first series N is ^{14}N, for the second series N is ^{17}O, and N is ^{19}F for the third series. K_N is the fixed constant for each N. In Eq. (3), g is the electronic g value, β is Bohr magneton, γ_N is the gyromagnetic ratio of N, h is the Planck constant and $\langle \hat{S}_z \rangle$ is the expectation value of S_z operator. The K_N values of ^{14}N, ^{17}O and ^{19}F are listed in Table III. With the calculated ρ_N of MO method and the corresponding $(a_N)_{obs}$ of Rerefences[9-26],

TABLE III

K_N of various nuclei (in gauss)[6]

Nuclei	^{1}H	^{14}N	^{17}O	^{19}F
$K_N = \frac{4\pi}{3} g \beta \gamma_N h \langle \hat{S}_z \rangle^{-1}$	1597.22	115.23	—216.32	1502.32

both K and $|\Phi_{2s}(R)|^2$ can be evaluated by the linear least squares method of Eqs. (4) and (5).

$$K = \frac{\sum_{i=1}^{n} (a_N)_{obs,i}\,(\varrho_N)_i}{\sum_{i=1}^{n} (\varrho_N)_i^2} \tag{4}$$

$$|\Phi_{2s}(R_N)|^2 = \frac{K}{K_N} \tag{5}$$

In (4), n is the number of data point in the related series. After K has been calculated, we may substitute it into Eq. (1) to calculate $(a_N)_{cal}$ of various radicals in each series. Consequently, the standard deviation, σ and the correlation coefficient, C, of each series can be calculated simultaneously by Eqs. (6) and (7).

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} [(a_N)_{obs,i} - (a_N)_{cal,i}]^2}{n-1}} \tag{6}$$

$$C = \frac{[n \sum_{i=1}^{n} (a_N)_{cal,i}\,(a_N)_{obs,i}] \cdot [\sum_{i=1}^{n} (a_N)_{cal,i}] - [\sum_{i=1}^{n} (a_N)_{obs,i}]}{\sqrt{n \sum_{i=1}^{n} (a_N)^2_{cal,i} - [\sum_{i=1}^{n} (a_N)_{cal,i}]^2} \cdot \sqrt{n \sum_{i=1}^{n} (a_N)^2_{obs,i} - [\sum_{i=1}^{n} (a_N)_{cal,i}]^2}} \tag{7}$$

III. RESULTS AND DISCUSSION

After completion of the SCF calculation, the linear least squares type correlation analysis was executed for each set of ρ_N's and $(a_N)_{obs}$'s in each series, as mentioned in the preceding section. In addition to the standard deviation and correlation coefficients of all cases, we calculated $(a_N)_{cal}$ and $\Delta a_N = |(a_N)_{cal} - (a_N)_{obs}|$ for each nucleus in each set, and compared Δa_N of our method with Δa_N of Pople et al. The number of better $(a_N)_{cal}$ in each case is defined by the number of smaller absolute value of Δa_N between our and Pople's results. All the statistical results of various cases are listed in Table IV.

(1) a_N *Calculation of* ^{14}N *in the First Series*

As shown in Table IV most of the results in the first series of ^{14}N are worse than the corresponding results of Pople's INDO. But as expected, the third set with separated β_{2p} ($\beta^{\pi}_{2p} \neq \beta^{\sigma}_{2p}$) and $Z'_H = 1.0$, gives the best results in the four sets of this series. We tablated the calculated $(a_N)_{cal}$'s of the third set in this work, $(a_N)_{cal}$'s of Pople's INDO, and $(a_N)_{obs}$'s of References[9-21] in Table V for comparison. The statistical calculation of the data in this Table shows that the result of this method in the third set of ^{14}N series is similar to or even better than the corresponding result of the conventional INDO-MO as shown in Table IV. The correlation coefficient, C, of this method is 0.8159, which is slightly worse than $C = 0.8198$ of Pople et al., but the standard

TABLE IV
Results of linear least square correlation analysis

Element	method Z_H'	β_{2p}	Number of data point	Standard Deviation (in gauss)	Correlation coefficient	Number of better a_N by comparasion with Pople's INDO
^{14}N	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.2	29	1.97	0.7984	12
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.2	29	2.82	0.5768	13
	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.0	29	1.89	0.8159	14
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.0	29	2.81	0.5783	13
	Pople INDO[6]		29	2.25	0.8198	
^{17}O	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.2	5	1.75	0.6681	5
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.2	5	1.97	0.5933	5
	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.0	5	1.72	0.6749	5
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.0	5	1.94	0.5998	5
	Pople INDO[6]		5	2.87	0.5188	
^{19}F	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.2	9	16.16	0.9557	6
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.2	9	13.98	0.9642	5
	$\beta\sigma_{2p} \neq \beta\pi_{2p}$	1.0	9	17.87	0.9455	6
	$\beta\sigma_{2p} = \beta\pi_{2p}$	1.0	9	15.92	0.9536	5
	Pople INDO[6]		9	22.22	0.9224	

TABLE V
a_N *of* ^{14}N *in the case of* $\beta_{2p}^{\pi} \neq \beta\sigma_{2p}$ *and* $Z'_H = 1.0$ *(in gauss)*

Radical		this work	INDO Pople	a_{obs}^{9-21}
Benzonitrile —		2.87	2.40	2.15
Phthalonitrile		2.35	1.90	1.80
Isophthalonitrile		1.66	1.30	1.82
Terephthalonitrile		2.53	2.00	1.81
1,2,4,5-Tetracyanobenzene		1.82	1.40	1.15
p-Nitrobenzonitrile —	— CN	1.23	1.10	7.15
	— NO	5.43	4.70	7.15
Nitrobenzene —		6.66	7.10	10.32
m-Dinitrobenzene —		3.43	0.50	4.68
p-Dinitrobenzene —		3.74	0.00	1.74
m-Fluoronitrobenzene —		6.52	6.60	12.60
p-Fluoronitrobenzene —		6.96	7.10	9.95
3,5-Difluoronitrobenzene —		6.41	6.10	8.09
Pyrazine —		9.01	8.30	9.21
N,*N*-Dihydropyrazine +		7.33	7.80	7.60
Pyridazine		7.34	7.70	5.90
s-Tetrazine —		6.65	5.80	5.28
1,5-Diazanaphthalene —		4.54	5.90	3.37
Phthalazine —		0.19	0.30	0.80
Quinoxaline —		6.54	7.30	5.64
Dihydroquinoxaline +		6.99	7.70	6.65
Phenazine —		6.50	7.20	5.14
1,4,5,8-Tetraazaanthracene —		3.04	3.30	2.41
p-Dicyanotetrazine —	RING	7.01	5.90	5.88
	— CN	—0.90	—0.90	—0.16
p-Nitrobenazaldehyde —		3.22	—0.50	5.83
p-Cyanobenzaldehyde —		1.58	1.00	1.40
4-Cyanopyridine —	RING	8.17	8.30	5.67
	— CN	2.89	2.70	2.33

deviation of this method is 1.89 gauss which is better than 2.25 gauss calculated by the data of Pople's INDO.[6]

(2) a_N *Calculation of* ^{17}O *in the Second Series*

In this series, all the results of four sets are better than the corresponding results of the conventional INDO method.[6] Similar to the first series of ^{14}N case, the result of the third set with $\beta^{\pi}_{2p} \neq \beta^{\sigma}_{2p}$ and $Z'_H = 1.0$ gives the best results among its four sets, and we give this result of the third set and the related data of References[6,22-23] in Table VI. As shown in this Table, all $(a_N)_{cal}$'s of ^{17}O in our method are better than the corresponding $(a_N)_{cal}$'s of Pople et al.[6] As for the calculated standard deviation and correlation coefficient in our calculation, $\sigma = 1.72$ gauss and $C = 0.6749$ are both better than the $\sigma = 2.87$ gauss and $C = 0.5188$ calculated by the conventional INDO method.[6]

TABLE VI

a_N *of* ^{17}O *in the case of* $\beta_{2p}{}^{\pi} \neq \beta^{\sigma}_{2p}$ *and* $Z'_H = 1.0$ *(in gauss)*

Radical	this work	Pople INDO	$a_{obs}^{22,23}$
p-Benzosemiquinone —	9.78	8.70	9.53
1,4-Naphthosemiäuinone —	9.18	9.30	8.58
9,10-Anthrasemiquinone —	8.57	9.90	7.53
2,5-Dioxo-1,4-semiquinone ≡	4.81	3.60	4.57
Nitrobenzen —	5.64	4.30	8.84

(3) a_N *Calculation of* ^{19}F *in the Third Series*

Similar to the second series, all the results of the four set calculations in the third series for ^{19}F are better than the corresponding result of Pople et al.[6] As shown in the last section of Table IV, the calculated standard deviation, correlation coefficients, and the numbers of better (a_N)'s (or smaller $\Delta a_N)$'s) by comparison of our calculation and Pople's data, are all in favor of our method, no matter what type of parameters we selected. Among the results of our calculations, the second set with single β_{2p} (or $\beta^{\pi}_{2p} = \beta^{\sigma}_{2p} =$

TABLE VII

a_N *of* ^{19}F *in the case of single* β_{2p} *and* $Z'_H = 1.2$ *(in gauss)*

Radical		this work	Pople INDO	$a_{obs}^{11,13,24,25,26}$
Fluoromethyl		61.97	71.30	64.30
Difluoromethyl		67.37	87.10	84.20
Trifluoromethyl		61.71	59.50	142.40
Monofluoroacetamide		63.75	34.40	54.60
Difluoroacetamide	1′	52.50	31.50	75.00
Difluoroacetamide	1	56.21	39.00	75.00
m-Fluoronitrobenzene —		—2.46	—4.00	—3.70
p-Fluoronitrobenzene —		5.71	6.30	8.41
3,5-Difluoronitrobenzene —		—2.25	—3.80	—2.73

$= \beta_{2p}$) and $Z'_H = 1.2$ gives the best results. In this set $\sigma = 13.89$ gauss and $C = 0.9642$, both of which are much better than $\sigma = 22.22$ gauss $C = 0.9224$ of Pople et al. By means of comparison, we listed the $(a_N)_{cal}$'s of our second set in ^{19}F series and the related data of Rerefences[6,11,13,24,25,26] in Table VII.

(4) Discussion and Conclusion

Our results shown in the three preceding paragraphes indicate that most of them are reliable and successful. Although the results of the first, second and fourth sets in the series of ^{14}N are not as good as we expected, when $\beta^{\pi}_{2p} \neq \beta^{\sigma}_{2p}$ and $Z'_H = 1.0$ are used in our third set, the improvement of our method is very prominent. In which, the calculated correlation coefficient, C, is 0.8159 which is only 0.0039 lower than People's value, but our standard deviation, σ, is 1.86 gauss which is better than People's σ by 0.36 gauss. All results of the series of ^{17}O are better than the related results of Pople et al. In which, the best calculation is the third set with $\beta^{\pi}_{2p} = \beta^{\sigma}_{2p}$ and $Z'_H = 1.0$. Due to satisfactory results of the third sets of both ^{14}N and ^{17}O, one can make the following two conclusions: (1) $Z'_H = 1.0$, which was successfully applied to a calculation of ^{1}H in our earlier work,[2-4] is also successfully applied to the a_N's of ^{14}N and ^{17}O calculations of organic free radicals in this work. (2) The separation of β^{π}_{2p} and β^{σ}_{2p} mentioned in our recent papers[7-8] is also a reasonable suggestion for the compounds of N and O with multiple bond in the open shell problems of free radicals.

Similar to the cases of ^{17}O, all the results of four sets in the ^{19}F series are better than the corresponding result of the conventional INDO. The best result within the four sets of ^{19}F is quite different from the cases of ^{14}N and ^{17}O. The second set with single β_{2p} and $Z'_H = 1.2$ is the best set among the four sets in ^{19}F series. The unusual results obtained in the ^{19}F series may be due to the following reasons: (1) Since fluorine usually forms a single bond in the molecule, the separation of bond parameters between β^{π}_{2p} and β^{σ}_{2p} is not necessary. (2) σ bond is usually stronger than π bond and consequently $\beta^{\sigma}_{2p} > \beta^{\pi}_{2p}$ in an ordinary case. But the calibrated β^{σ}_{2p} and β^{π}_{2p} of fluorine atom in this work are 49.232 and 55.300 ev, as shown in Table I. This abnormal $\beta^{\sigma}_{2p} < \beta^{\pi}_{2p}$ relation may not be a good choice for our MO calculation. (3) $Z'_H = 1.2$ used for hydrogen in the ^{19}F series usually gives a better result due to the large polar effect of the most electronagative fluorine element. When the electronic charge of hydrogen shifts to the other part of the molecule, the larger Z'_H ($Z'_H = 1.2$) with smaller AO of hydrogen may be more reasonable than the molecule with smaller Z'_H in the fluorine series.

From all the above results it is found that the open shell MO calculation of various series of radicals in this work is quite reliable from the semi-empirical point of view. Most of the results in this paper are better than the corresponding results of the conventional INDO method. The success of the calculation here is an additional evidence supporting the correctness and usefulness of the original s-p separation idea in modification of the INDO-MO problem.

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SAŽETAK

Proračun konstanti hiperfinog sprezanja atoma ^{14}N, ^{17}O i ^{19}F u kemijskim okolinama

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Pretpostavljajući da su konstante hiperfine strukture atoma ^{14}N, ^{17}O i ^{19}F proporcionalne spinskoj gustoći smještenoj u 2s orbitali, dobiveni su vrlo dobri rezultati za velik broj slobodnih radikala primjenom modificirane INDO metode.