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Theoretical Calculations of The Magnetic Susceptibility in Some Organic Molecules

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Magnetic susceptibility of a number of sizeable organic molecules is calculated by using the model of additivity of localized molecular fragments. The results are in a good agreement with available experimental data.

The last several years have witnessed significant advances in both experimental and theoretical studies of electronic structure and molecular properties of large molecules. The ideas of transferrability and additivity of charge distributions, corroborated by various methods of localization of molecular orbitals[1] have been applied to calculations of the magnetic properties of the localized molecular fragments and molecules.

The possibility of theoretical interpretation of the molecular properties as a sum of contributions arising from different parts of a molecule in terms of localized molecular orbitals was thoroughly discussed in[2–7].

This article will be primarily concerned with prediction of values of magnetic susceptibility of large molecules.

It has been shown that within the framework of approximation of the additivity of localized molecular fragments[8,9], the traditional variational procedure[10,11] can be successfully used for the evaluation of the magnetic properties of the second order. Some of these results are presented in Table I.

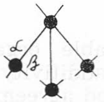
The possibilities of the applied approach are to be discussed, not its accuracy. Therefore, one cannot find a comparision of the theoretical values of χ and σ with some of the best literature data[12,13] in Table I, which are not far from our values. The trend of changes in both calculated and the observed values is the same. The nature of χ, χ^d, χ^p, σ, σ^d and σ^p is not to be discussed, for it had been done in various works, for instance[14–17]. It must be emphasized that the main idea of this investigation has been to find a reasonable approximation which would allow a fairly accurate evaluation of magnetic susceptibility (χ) and nuclear shielding constants (σ) of very large molecules that cannot be studied at present by ab initio or semiempirical methods.

In the framework of the traditional variational procedure[10,11] the wavefunction of the electronic system in the presence of external magnetic field can be written as:

$$\psi = \psi_0 (1 + \vec{g}\vec{H} + \ldots), \tag{1}$$

TABLE I

Theoretical and experimental data for magnetic susceptibility (χ) and proton shielding constants (σ) of small molecules[a]

Molecule	$-\chi^{\text{Theor.}}$	$-\chi^{\text{Exptl.}}$	$\sigma^{\text{Theor.}}$	$\sigma^{\text{Exptl.}}$
NH_3	13.961	16.3 ± 0.8[b]	27.585	30.68 ± 0.6[c]
CH_4	15.498	17.4 ± 0.8[b]	28.747	30.63 ± 0.6[c]
H_2O_2	17.359	17.7[b]	26.938	—
PH_3	25.260	26.23 ± 0.8[d]	29.788	29.1[d]
C_2H_6	27.15	26.8 ± 0.8[d]	28.654	29.72 ± 0.2[e]
CH_3NH_2	26.600	27.0[f]	CH_3 28.586 28.268	28.24 ± 0.2[e]
			NH_2 25.721	—
C_3H_8	37.806	40.5[f]	CH_3 28.657	29.58[g]
			CH_2 28.532	29.20[g]
$C_2H_5NH_2$	36.926	—	—	—
			α 26.612	—
$P(CH_3)_3$ 	55.723		β 29.267	—

[a] 10^{-6} c.g.s. units ($-\chi$ in 10^{-6}cm^3 mol^{-1} units).

[b] B. D. Appleman and B. P. Dailey, in *Adv. of Magn. Reson.* **7** (1974) 231.

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[e] R. M. Aminova, N. I. Zoroatskaya, and Yu. Yu. Samitov, *J. Magn. Res.* **33** (1979) 497.

[f] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High resolution nuclear magnetic resonance spectroscopy.* v**1**. Pergamon Press, Oxford, 1969.

[g] E. U. Dayan and G. Widenlocher, *Comp. Rend.* **257** (1963) 883.

where ψ_0 — is an unperturbated wavefunction of the electronic system that can be chosen as a linear combination of atomic orbitals φ_j:

$$\psi_0 = \sum_j C_j \varphi_j \tag{2}$$

and $\vec{g}$ — is the additional variational coordinate function.

The expressions for the components of the magnetic susceptibility ($\chi_{\alpha\beta}$) and nuclear magnetic shielding tensors ($\sigma_{\alpha\beta}$) are:

$$\chi_{\alpha\beta} = -\frac{e^2}{4mc^2}\langle\psi_0|\sum_k \vec{r}_k^{\,2}\,\delta_{\alpha\beta} - r_{k\alpha} r_{k\beta}|\psi_0\rangle + 2\langle\psi_0|\sum_k M_{k\alpha}\, g_\beta|\psi_0\rangle + \frac{\hbar^2}{m}\langle\psi_0|\nabla g_\alpha|\nabla g_\beta|\psi_0\rangle; \tag{3}$$

$$\frac{e^2}{2mc^2}\langle\psi_0|\sum_k \frac{\vec{r}_k\,\vec{r}_k\,\delta_{\alpha\beta} - r_{k\alpha} r_{k\beta}'}{r_k^3}|\psi_0\rangle - \langle\psi_0|\sum_k \frac{M_{k\alpha}}{r_k^3}\, g_\beta'|\psi_0\rangle, \tag{4}$$

where

$$M_{k\alpha} = \frac{e\hbar}{2mci}\,[\vec{r}_k \times \vec{\nabla}]_\alpha. \tag{5}$$

The atomic basis set of spherical Gaussian functions has been used to avoid computation difficulties in evaluating the multicentered integrals written in the above (3)—(4) equations for the arbitrary origin of the coordinate system:

$$\varphi_j = \sum_i a_i \exp\{-a_i(\vec{r} - \vec{A}_i)^2\}. \tag{6}$$

One can obtain the unpertubated wavefunction of any localized molecular fragments of interest since the methods of accurate definition of ψ_0 and φ_j for small molecules are well developed now.

It should be noted that for the electronic systems with the axial symmetry, such as σ-bonds, lone pairs, etc., in formulas (1), (3) and (4) can be selected (as it has been shown in[8,9]), as a linear combination of different degrees of Cartesian coordinates:

$$\vec{g} \sim \sum_i b_i x_i^l y_i^m z_i^k \tag{7}$$

By omitting the details of evaluation of variational parameters b_i in (7)-discussed in[8,9], one must solve the question of transferrability both of the wavefunction of localized molecular fragment and of its molecular properties for the compounds of the same homologous rates.

From the results of the calculations presented in Table II it can be concluded that for the similar localized molecular fragments of different molecules the values of χ and σ are not changed considerably.

The same conclusion have been made for the values of χ and σ, calculated by means of ψ_0, found by G. Leroy and D. Peeters (see references in[1]), in the framework of the method of localization suggested by Magnasco and Perico for the same compounds[19]. Thus, it can be assumed that there is no influence of the method of localization of ψ_0 upon the values of χ and σ. But as it was shown in ref. 20, the values of χ and σ strongly depend upon the bond lengths rather than upon the accuracy of the method of calculation of ψ_0. It must be also emphasized that the wavefunction can be calculated either by ab initio or some of the semiempirical methods, but the coincidence of geometry of the molecule with the experiment must be taken into account.

One of the serious problems of the theory of magnetic properties of the second order is the dependence of the calculated values upon garge origin.

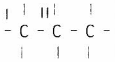
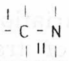
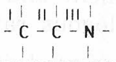
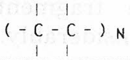
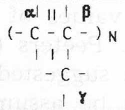
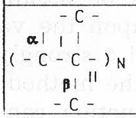
In the previous works[20,21] it was found that the value of χ and σ of localized molecular fragments calculated in the framework of the traditional variational procedure are garge independent even for limited atomic basis sets.

The calculated values of χ with the corresponding bond lenghs for some localized molecular fragments presented in Table III are recommended for utilization.

Using the approximation of additivity, the molar magnetic susceptibility of some saturated hydrocarbons, amines, alcohols and bioorganic molecules have been calculated. These values are given in Tables IV, V, VI, VII. The

TABLE II

Magnetic susceptibility of σ— bonds in some molecules[a]

MOLECULE	C-H[18]	$-\chi$ C-C[18]	C-N	N-H
NH_3	-	-	-	3.530
CH_4	3.804	-	-	-
C_2H_6	3.801	3.758	-	-
C_3H_8 	I 3.807 II 3.800	3.758	-	-
CH_3NH_2 	I 3.800 II 3.800	-	3.457	3.532
$C_2H_5NH_2$ 	I 3.796 II 3.800 III 3.798	3.757	3.456	3.532
	3.799	3.745	-	-
	α 3.801 β 3.798 γ 3.844	I 3.758 II 3.759	-	-
	α 3.874 β 3.851	I 3.751 II 3.751	-	-

[a] See ref. »a« in Table I.

TABLE III

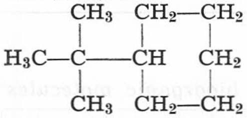
Molar susceptibility of localized molecular fragments

Fragment	C—H	C—C	C—N	N—H	P—H	P—C	O—O	O—H	C—O	L·p O	L·p N
$-\chi^a$	3.80	3.76	3.46	3.53	6.21	3.46	2.15	3.32	3.41	1.72	3.1
bond length Å	1.09	1.54	1.474	1.014	1.42	1.85	1.475	0.95	1.43	—	—

L.p. — lone pair; [a]See ref. »a« in Table I

TABLE IV

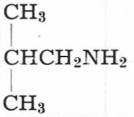
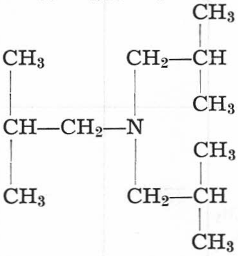
Molar magnetic ussceptibility of saturated hydrocarbons[a,f]

Molecule	$-\chi^{\mathrm{Theor.}}$	$-\chi^{\mathrm{Exptl.}}$
$CH_3(CH_2)_3CH_3$	61.41	—
$(CH_3)_2CHCH_2(CH_3)_2$	72.92	—
$CH_3(CH_2)_4CH_3$	72.95[18]	74.6
$CH_3CHCH_2CH(CH_3)_2$	84.42	—
$CH_3(CH_2)_5CH_3$	84.44	—
$(CH_3)_2CH(CH_2)_3CH_3$	85.58[18]	86.24
$(CH_3)_2CHCH_2CH(CH_3)_2$	85.93[18]	86.97
$CH_3(CH_2)_6CH_3$	95.95	96.63
$CH_3(CH_2)_7CH_3$	107.46	—
$CH_3(CH_2)_8CH_3$	118.95	—
	115.18	115.09
$CH_3(CH_2)_{10}CH_3$	141.99	—
$CH_3(CH_2)_{13}CH_3$	176.53	—
$CH_3(CH_2)_{16}CH_3$	211.07	—
$CH_3(CH_2)_{17}CH_3$	222.58	—
$CH_3(CH_2)_{20}CH_3$	257.12	—
$CH_3(CH_2)_{30}CH_3$	372.24	—

[a,f] See ref. »a« and »f« in Table I.

TABLE V

Molar magnetic susceptibility of the amines[a,f]

Molecule	$-\chi^{\mathrm{Theor.}}$	$-\chi^{\mathrm{Exptl.}}$
$CH_3CH_2NHCH_2CH_3$	56.7	56.8
 $\underset{CH_3}{\overset{CH_3}{CH}}CH_2NH_2$	56.73	58.9
$CH_3(CH_2)_4NH$	68.24	69.4
$(C_2H_5)_3N$	82.85	81.4
$(HOCH_2CH_3)_3N$	88.70	91.33
$C_7H_{17}N$	94.36	—
$(C_3H_7)_3N$	117.39	—
$(C_4H_9)_3N$	151.92	—
$CH_3(CH_2)_{10}CH_2NH_2$	151.99	—
	155.73	156.8

[a,f] See ref. »a« and »f« in Table I.

TABLE VI

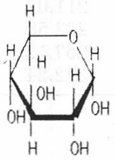
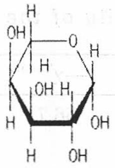
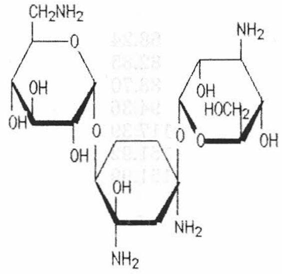
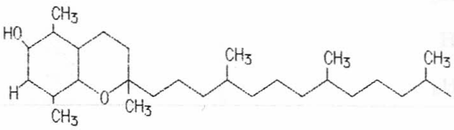
Molar magnetic susceptibility of alcohols[a,f]

	$-\chi^{\mathrm{Theor.}}$	$-\chi^{\mathrm{Exptl.}}$
$CH_3(CH_2)_2OH$	44.84	45.18
$CH_3(CH_2)_3OH$	56.35	56.54
$CH_3(CH_2)_4OH$	67.86	67.5
$C_6H_{11}OH$	75.92	73.4
$CH_3(CH_2)_5OH$	79.38	79.2
$CH_2(CH_2)_5CHOH$	87.04	—
$CH_3(CH_2)_6CH_2OH$	102.40	102.65
$CH_3(CH_2)_9OH$	125.43	—
$CH_3(CH_2)_{10}CH_2OH$	148.45	147.70
$CH_3(CH_2)_{11}CH_2OH$	159.96	—

[a,f] See ref. »a« and »f« in Table I.

TABLE VII

Molar magnetic susceptibility of some bioorganic molecules[a,f]

Molecule	$-\chi^{\mathrm{Theor.}}$	$-\chi^{\mathrm{Exptl.}}$
	83.9	84.8
	85.9	85.7
	258.26	-
	339.29	-

[a,f] See ref. »a« and »f« in Table I.

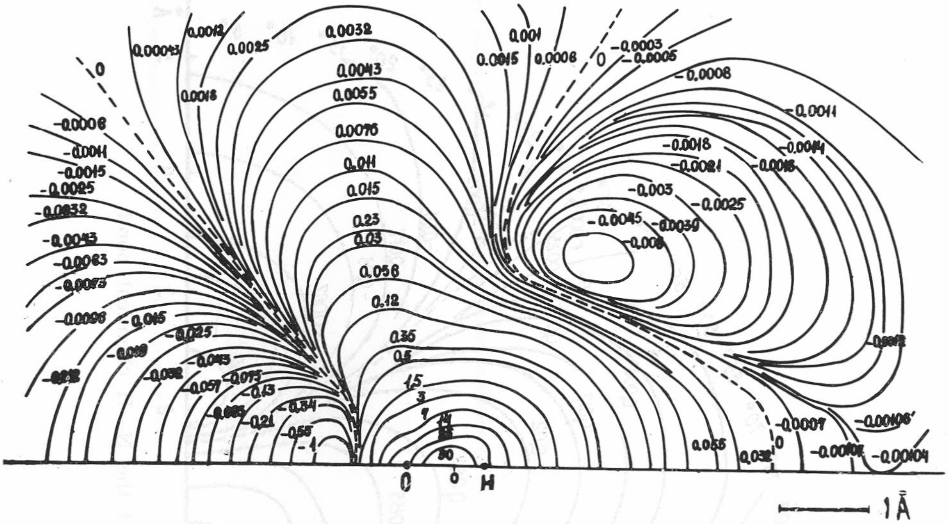
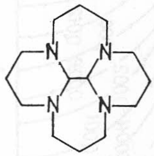


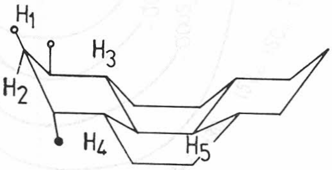
Figure 1. Diagram of the isoscreening lines of the O—H chemical bond.

TABLE VIII

Interpretation of proton chemical shifts of tetracyclic tetramines by means of diagrams of isoscreening lines

Experiment[22]		Theory
$\Delta\,\delta\,(H_1 - H_2)$	$= 0.75$	0.393
$\Delta\,\delta\,(H_3 - H_4)$	$= 2.20$	1.6
$\Delta\,\delta\,(H_2 - H_5)$	$= 1.44$	0.8





theoretical values of χ are presented for the first time in literature and they coincide excellently with the observed data. Thus, in any further studies one can use the values of χ for the molecules as »markers« both in theoretical and experimental investigations.

Diagrams of isoscreening lines, calculated for the localized O—H, N—H, P—H and O—O chemical bonds are given in Figure 1, 2, 3, 4[9,20]. The dependence of these diagrams upon both the garge origin and the accuracy of the wavefunction is discussed in[20,21]. The interpretation of NMR data can be done with the help of the diagrams, as it was shown in[8,9].

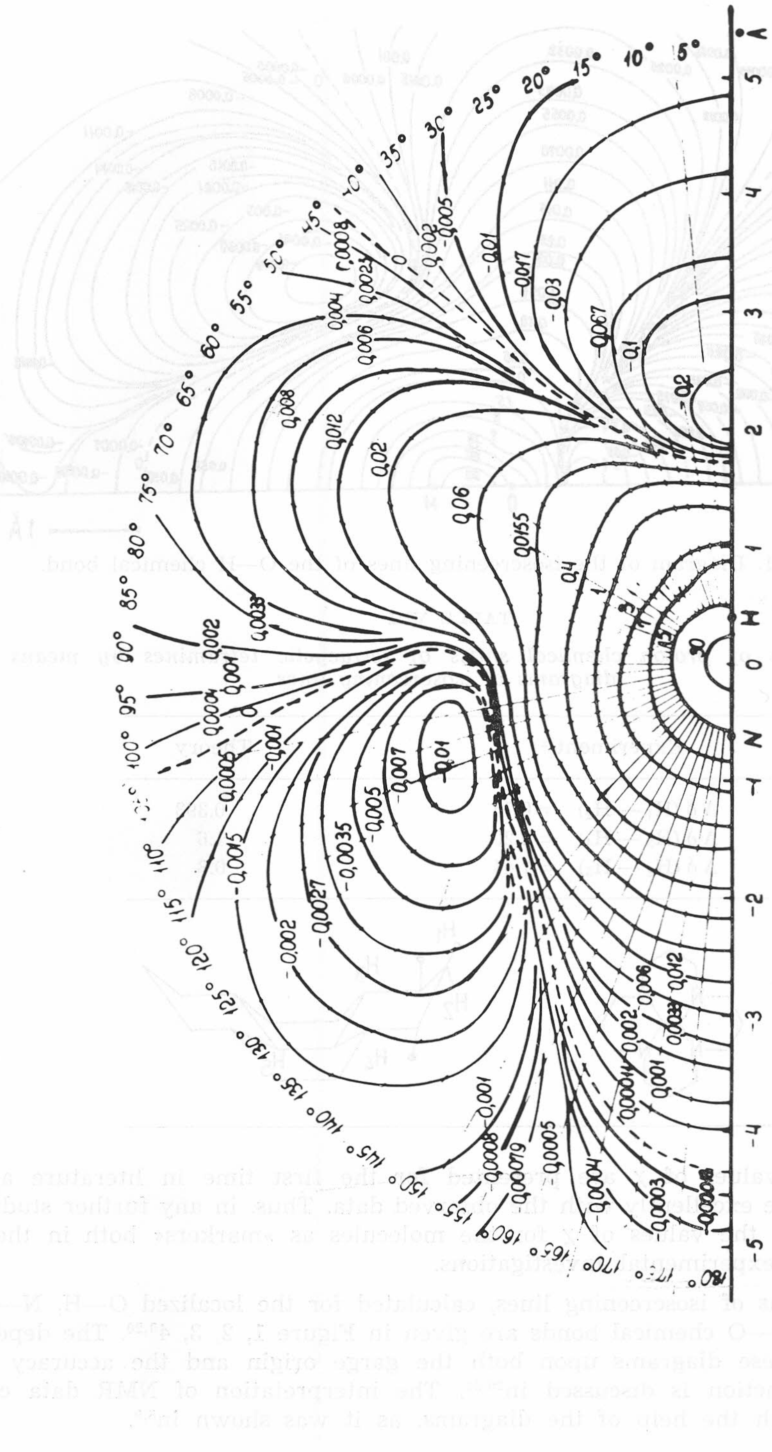


Figure 2. Diagram of the isoscreening lines of the N—H chemical bond.

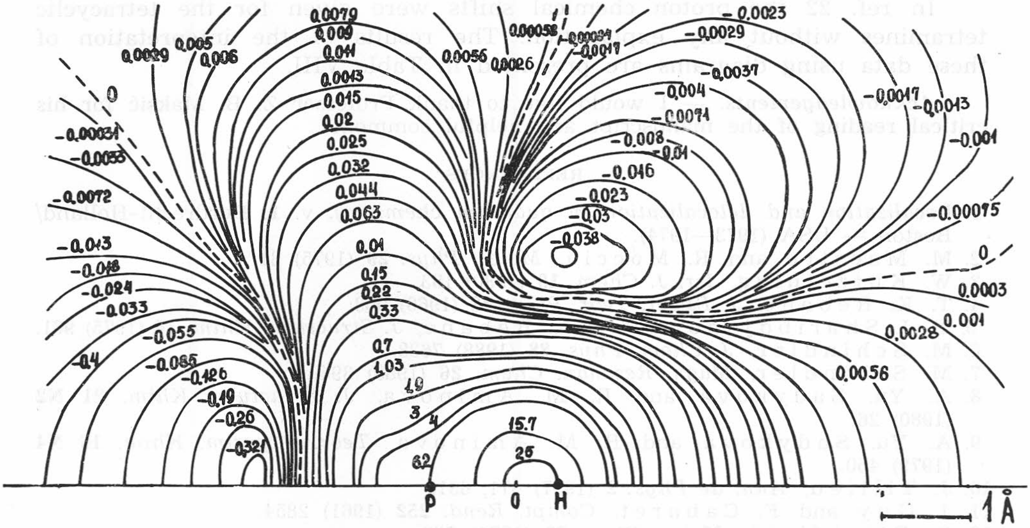


Figure 3. Diagram of the isoscreening lines of the P—H chemical bond.

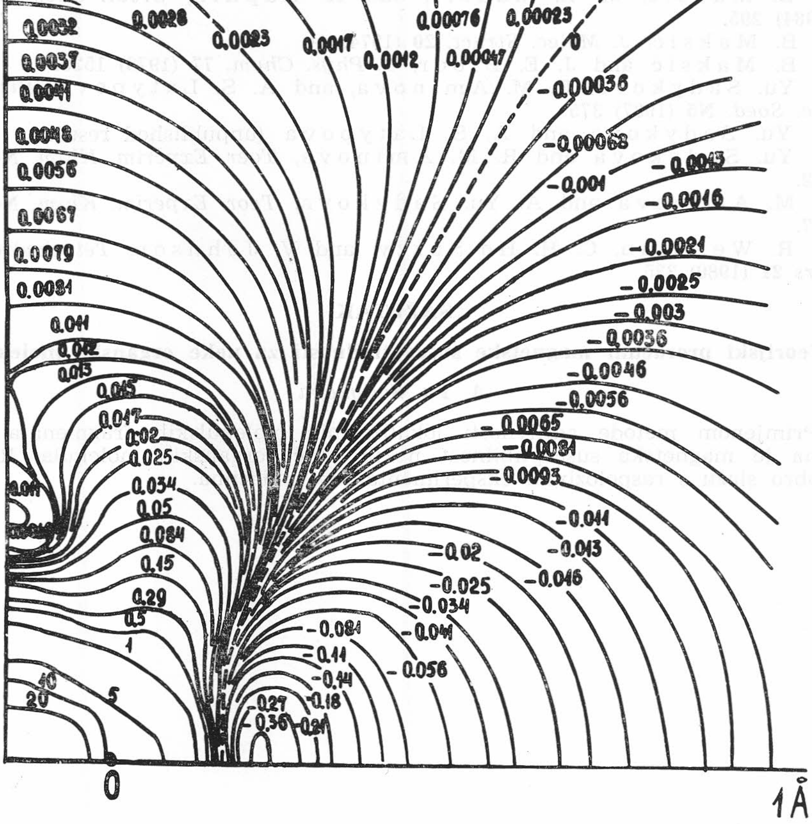


Figure 4. Diagram of the isoscreening lines of the O—O chemical bond.

In ref. 22 the proton chemical shifts were given for the tetracyclic tetramines without any explanation. The results of the intepretation of these data using diagrams are presented in Table VIII.

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SAŽETAK

Teorijski proračuni magnetske susceptibilnosti za neke organske molekule

A. Yu. Sadykova

Primjenom metode aditivnosti lokaliziranih molekulskih fragmenata proračunana je magnetska susceptibilnost nekih većih organskih molekula. Rezultati se dobro slažu s raspoloživim eksperimentalnim podacima.