

CCA-780

539.19:538.214

Note

## On the Additivity of the Molecular Second Moments of Charge and Diamagnetic Susceptibility

Z. B. Maksić

*Institute »Ruđer Bošković, 41001 Zagreb, Croatia, Yugoslavia*

Received February 5, 1973

It was shown that the application of the additivity rules [*Chem. Phys. Letters* **13** (1972) 571] may be very helpful for the determination of the sign of the  $g$  tensor.

Recently, a large number of experimental molecular quadrupoles, diamagnetic and paramagnetic susceptibilities and second moments of charge became available<sup>1</sup>. This immense pool of experimental data gave strong impetus for the theoretical treatment of these quantities on the semiempirical level<sup>2-4</sup>. The additivity of second moments was put forward first by Flygare *et al.*<sup>5</sup> who have shown that the second moment related to the out of the heavy atoms plane coordinate  $c$  is easily obtained by using simple empirical additivity rules. These rules were subsequently rationalised within the framework of the semiempirical CNDO/2 method where  $\langle c^2 \rangle$  second moments were calculated in the one-center approximation<sup>2</sup>. Flygare *et al.*<sup>6</sup> established recently an empirical scheme based on atomic dipoles which enables highly accurate estimates of second moments. This method takes into account the anisotropy of the electronic charge distribution in the vicinity of nuclei and also employs different parameters for the same atom in different moieties. We have shown<sup>7</sup> that the molecular second moments of electronic charge can be easily calculated, albeit not so accurate, by an additivity equation which employs only few parameters

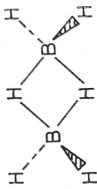

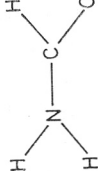
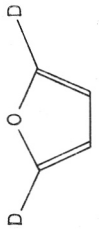
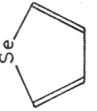
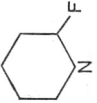
$$\langle 0 | v^2 | 0 \rangle = \sum_n^{\text{Atoms}} Z_n v_n^2 + \sum_p k_p n_p \quad (1)$$

where  $v$  denotes coordinates  $x$ ,  $y$  and  $z$  of the molecular system of coordinates\*,  $|0\rangle$  is the ground state Slater determinant,  $Z_n$  is atomic number of the nucleus  $n$ ,  $n_p$  is a number of atoms belonging to the  $p$ -th period of the Mendeleev system of elements and  $k_p$  is a constant characterising  $p$ -th period. It is seen from the formula (1) that the atomic contribution to the molecular second moment is not only isotropic but it is also constant for all atoms belonging to the same period. The values  $k_p$  found earlier<sup>7</sup> read as follows (in  $10^{-16} \text{ cm}^2$ ):

\*  $v$  refers frequently to the principal inertial axes coordinates  $a$ ,  $b$  and  $c$ .



TABLE I (contd.)

Molecule		Calcd.	Exp.	Calcd.	Exp.
	$\Sigma Z_n x_n^2$	= 4.3		$\chi_{xx}^d$	= -110.8 <sup>13</sup>
	$\Sigma Z_n y_n^2$	= 2.0		$\chi_{yy}^d$	= -122.7
	$\Sigma Z_n z_n^2$	= 16.8		$\chi_{zz}^d$	= -56.0
	$\Sigma Z_n a_n^2$	= 40.1	45.0 ± 0.8	$\chi_{aa}^d$	= -118.8
	$\Sigma Z_n b_n^2$	= 15.4	21.2 ± 0.8	$\chi_{bb}^d$	= -223.6
	$\Sigma Z_n c_n^2$	= 3.2	9.0 ± 0.8	$\chi_{cc}^d$	= -275.3
	$\Sigma Z_n a_n^2$	= 25.2**	28.3 ± 0.9	$\chi_{aa}^d$	= -53.9
	$\Sigma Z_n b_n^2$	= 5.5	8.4 ± 0.9	$\chi_{bb}^d$	= -137.4
	$\Sigma Z_n c_n^2$	= 0	4.0 ± 0.9	$\chi_{cc}^d$	= -160.8
	$\Sigma Z_n a_n^2$	= 32.6	37.4 ± 0.7 <sup>f</sup>	$\chi_{aa}^d$	= -182.4
	$\Sigma Z_n b_n^2$	= 31.4	37.7 ± 0.7	$\chi_{bb}^d$	= -187.5
	$\Sigma Z_n c_n^2$	= 0	6.9 ± 0.7	$\chi_{cc}^d$	= -320.7
	$\Sigma Z_n a_n^2$	= 78.2	86.5 ± 3.4 <sup>f</sup>	$\chi_{aa}^d$	= -241.4
	$\Sigma Z_n b_n^2$	= 48.3	47.9 ± 3.4	$\chi_{bb}^d$	= -402.2
	$\Sigma Z_n c_n^2$	= 0	9.8 ± 3.4	$\chi_{cc}^d$	= -573.1
	$\Sigma Z_n a_n^2$	= 98.7	105.7 <sup>h</sup>	$\chi_{aa}^d$	= -277.9
	$\Sigma Z_n b_n^2$	= 49.9	57.2 ± 5.1	$\chi_{bb}^d$	= -484.9
	$\Sigma Z_n c_n^2$	= 0	8.7	$\chi_{cc}^d$	= -696.6

\* The experimental data are taken from the ref. (1) if it is not stated otherwise; \*\* A planar structure of formamide was assumed.

p	0	1	2	3	4
$k_n$	0.2	1	2.5	3.5	5.5

Here we give some more evidence for the additivity of the second moments in the sense of the equation (1) and for the additivity of the closely related diamagnetic susceptibility. We shall discuss in particular the potential use of the eqn. (1) in determining the sign of the  $g$  tensor. The earlier approaches used additivity of  $\langle c^2 \rangle$  second moments<sup>5</sup> or semiempirical CNDO/2 method<sup>4</sup>. The second moments obtained by the eqn. (1) and the diagonal elements of the diamagnetic susceptibility tensor

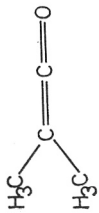
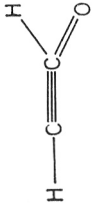
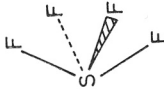
$$\chi_{aa}^d = (Le^2/4mc_0^2) \langle o | b^2 + c^2 | o \rangle^*$$

are compared with some *ab initio* results and the most recent experimental data in the Table I. The agreement with experiment and *ab initio* calculations is very good, the exception being ozone. This discrepancy indicates that either some special bonding features are present in this molecule or perhaps that the experimental results should be reinvestigated. The second moments in 2-fluoropyridine are not unambiguously determined by the experiment due to the indeterminacy in sign of the  $g$  values<sup>8</sup>. The set of second moments presented in Table I corresponds to the diagonal  $g$  components — 0.088, — 0.041 and 0.023 for  $g_{aa}$ ,  $g_{bb}$  and  $g_{cc}$  respectively. The alternative choice of sign in  $g$  would lead to the negative  $\langle c^2 \rangle = -10.7$  value and could be rejected as physically unacceptable since  $\langle v^2 \rangle$  is always positive. Nevertheless the fine agreement obtained for the former set of second moments illustrates the potential capability of the eqn. (1) to make a proper choice of sign, what could be very useful in cases where both sets of second moments are physically acceptable. If the bulk magnetic susceptibility is not known then only the anisotropies in the second moments could be experimentally obtained. The anisotropies for dimethylketene, propynal and  $SF_4$  are listed in the Table II. The agreement with experiment for propynal and  $SF_4$  is satisfactory. There are two possible sets of second moments for dimethylketene<sup>9</sup>. The corresponding values are close to each other and it is hard to make a choice. Despite of that it seems that the set  $g < 0$  is slightly preferable.

To conclude, one can say that the present results provide further support of the simple additivity formula (1). It gives also a very simple criterion for the choice of the sign of  $g$  values. Therefore it is not necessary to perform semiempirical calculation of second moments for this purpose as we recommended earlier<sup>4</sup> since the straightforward application of the formula (1) will suffice if the two possible sets are not too close to each other. It should be mentioned that the second moments calculated by the eqn. (1) could be easily transformed to the gauge invariant values<sup>10</sup> simply by transforming the terms  $\sum_n Z_n v_n^2$  to the center of the positive charge of a molecule.

\* The remaining two expressions are easily obtained by the cyclic permutation of the coordinates while the constants have their usual meaning.

TABLE II  
Comparison between the Calculated and Experimental Anisotropies in Second Moments

Molecule	$\Sigma Z_n a_n^2$ $\Sigma Z_n b_n^2$ $\Sigma Z_n c_n^2$	Calcd. $\langle a^2 \rangle - \langle b^2 \rangle =$ $\langle b^2 \rangle - \langle c^2 \rangle =$ $\langle c^2 \rangle - \langle a^2 \rangle =$	$g < 0$	Exp.	$g > 0$
	$\Sigma Z_n a_n^2 = 70.3$ $\Sigma Z_n b_n^2 = 36.9$ $\Sigma Z_n c_n^2 = 3.2$	$\langle a^2 \rangle - \langle b^2 \rangle = 33.4$ $\langle b^2 \rangle - \langle c^2 \rangle = 33.7$ $\langle c^2 \rangle - \langle a^2 \rangle = -67.1$	$33.8 \pm 1.0^a$ $34.4 \pm 0.9$ $-68.2 \pm 1.1$		$31.3 \pm 1.2^9$ $34.1 \pm 0.9$ $-65.9 \pm 1.1$
	$\Sigma Z_n a_n^2 = 56.9$ $\Sigma Z_n b_n^2 = 5.0$ $\Sigma Z_n c_n^2 = 0$	$\langle a^2 \rangle - \langle b^2 \rangle = 51.9$ $\langle b^2 \rangle - \langle c^2 \rangle = 5.0$ $\langle c^2 \rangle - \langle a^2 \rangle = -56.9$		$51.6 \pm 0.5^{18}$ $4.3 \pm 0.7$ $-55.9 \pm 0.4$	
	$\Sigma Z_n a_n^2 = 48.6$ $\Sigma Z_n b_n^2 = 25.8$ $\Sigma Z_n c_n^2 = 10.1$	$\langle a^2 \rangle - \langle b^2 \rangle = 22.8$ $\langle b^2 \rangle - \langle c^2 \rangle = 15.7$ $\langle c^2 \rangle - \langle a^2 \rangle = -38.5$		$24.3 \pm 0.9^{19}$ $17.0 \pm 1.3$ $-41.3 \pm 1.1$	

*Acknowledgment.* I would like to thank to Dr. W. Hüttner for critical reading of the manuscript and useful comments.

## REFERENCES

1. W. H. Flygare and R. C. Benson, *Mol. Phys.* **20** (1971) 225, and the references cited therein.
2. J. E. Bloor and Z. B. Maksić, *Mol. Phys.* **22** (1971) 351; Z. B. Maksić and J. E. Bloor, *Croat. Chem. Acta* **44** (1972) 435.
3. J. R. Rabinowitz and R. Rein, *Int. J. Quant. Chem.* **6** (1972) 669; R. Rein, G. R. Pack and J. R. Rabinowitz, *J. Magn. Res.* **6** (1972) 360.
4. J. E. Bloor and Z. B. Maksić, *J. Chem. Phys.* **57** (1972) 3572.
5. R. P. Blickensderfer, Y. H. S. Wang, and W. H. Flygare, *J. Chem. Phys.* **51** (1971) 3196.
6. T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Am. Chem. Soc.* **94** (1972) 331.
7. Z. B. Maksić and J. E. Bloor, *Chem. Phys. Lett.* **13** (1972) 571; Z. B. Maksić and J. E. Bloor, *J. Phys. Chem.* (in press).
8. D. Sutter, *Z. Naturf.* **26a** (1971) 1644.
9. D. Sutter, L. Charpentier, and H. Dreizler, *Z. Naturf.* **27a** (1972) 597.
10. L. Weisenthal and A. M. de Graf, *Phys. Rev. Lett.* **27** (1971) 470.
11. *Ab initio* results: C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* **48** (1969) 407.
12. *Ab initio* results: R. Bonacconsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* **48** (1968) 1500.
13. *Ab initio* results: E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.* **94** (1972) 4461.
14. E. Hamer, D. H. Sutter, and H. Dreizler, *Z. Naturf.* **27a** (1972) 1159.
15. H. L. Tigelaar and W. H. Flygare, *J. Am. Chem. Soc.* **94** (1972) 343.
16. B. Bak, E. Hamer, D. H. Sutter, and H. Dreizler, *Z. Naturf.* **27a** (1972) 705.
17. W. Czieslik, D. Sutter, H. Dreizler, C. L. Norris, S. L. Rock, and W. H. Flygare, *Z. Naturf.* **27a** (1972) 1691.
18. R. C. Benson, R. S. Scott, and W. H. Flygare, *J. Phys. Chem.* **73** (1969) 4359.
19. R. G. Stone, H. L. Tigelaar, and W. H. Flygare, *J. Chem. Phys.* **53** (1970) 3947.

## IZVOD

**O aditivnosti drugih momenata elektronskog naboja molekula i dijamagnetske susceptibilnosti**

Z. B. Maksić

Pokazano je da primjena pravila aditivnosti [*Chem. Phys. Letters* **13** (1972) 571] može pomoći kod određivanja predznaka g-tenzora.

INSTITUT »RUĐER BOSKOVIĆ«  
41000 ZAGREB

Primljeno 5. veljače 1973.