

## Empirical Calculation of the Diamagnetic Susceptibility of Molecules

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Recent development of experimental microwave spectroscopy<sup>1</sup> and *ab initio* computational techniques based on Gaussian atomic functions<sup>2</sup> have made available values of diamagnetic susceptibilities and individual second moments of the electronic charge distributions for a large number of molecules. The analysis of the experimental results have led Blickensderfer *et al.*<sup>3</sup> to the development of empirical rules for the out-of plane  $\langle c^2 \rangle$  second moments for planar molecules involving first row atoms and hydrogens. These empirical rules were later rationalized within the zero-differential overlap approximation at the CNDO/2 level of sophistication<sup>4</sup>. Subsequently, it was shown that similar additivity rules hold for in plane second moments  $\langle a^2 \rangle$  and  $\langle b^2 \rangle$  if they are calculated first in the point charge approximation. Namely, the second moment  $\langle a^2 \rangle$  calculated within ZDO approximation takes the following form:


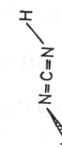
$$\langle a^2 \rangle \cong \sum_A \sum_{\mu} P_{\mu\mu} \langle \Phi_{\mu} | a^2 | \Phi_{\mu} \rangle \quad (1)$$



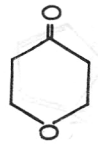
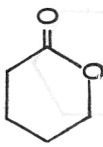
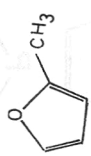
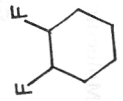
where  $P_{\mu\mu}$  is the conventional diagonal element of the bond order matrix  $P_{\mu\mu} = 2 \sum_{i=1}^{\text{occ.}} c_{\mu}^2$ , and  $\Phi_{\mu}$  is STO atomic orbital centered on the nucleus A. The sums over A and  $\mu$  are extended over nuclei and  $\Phi_{\mu}$  orbitals respectively. Introducing a transformation of coordinates  $a = a_A + a_A(\mu)$ , where  $a_A$  is the coordinate of the nucleus A measured from the center of mass of a molecule and  $a_A(\mu)$  is the coordinate of an electron  $\mu$  measured from the nucleus A, the second moment (1) is broken down to two terms


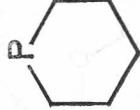

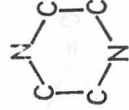
$$\langle a^2 \rangle \cong \sum_A \sum_{\mu} P_{\mu\mu} a_A^2 + \sum_A \sum_{\mu} P_{\mu\mu} \langle \Phi_{\mu} | a_A^2(\mu) | \Phi_{\mu} \rangle \quad (2)$$

The first term is large and represents the value of the second moment in the point charge approximation. Assuming that there is not appreciable intramolecular charge transfer, the sum  $\sum_{\mu} P_{\mu\mu}$  is equal to the number of electrons in the neutral atom, *i. e.*  $\sum_{\mu} P_{\mu\mu} = Z_A$ . The second term in the eq. (2) arises due to the spatial extension of atomic orbitals. Interestingly enough, the sum  $\sum_{\mu} P_{\mu\mu} \langle \Phi_{\mu} | a_A^2(\mu) | \Phi_{\mu} \rangle$  is approximately constant for all atoms belonging to

TABLE I  
 Comparison between empirical second moments of the electronic charge distributions  
 and diamagnetic susceptibilities and the corresponding *ab initio* and experimental  
 values\*

Molecule	Second Moments			Diamagnetic Susceptibilities	
	Point charge approxn.	Additivity formula	<i>Ab initio</i> or exptl.	Additivity formula	<i>Ab initio</i> or exptl.
HBS	$\langle x^2 \rangle = 15.2$	18.9	19.1 <sup>a</sup>	$\chi_{  }^d = -31.4$	-38.2 <sup>a</sup>
	$\langle y^2 \rangle = 0$	3.7	4.5	$\chi_{\perp}^d = -95.9$	-100.1
CS	$\langle z^2 \rangle = 10.3$	13.8	14.0 <sup>a</sup>	$\chi_{  }^d = -29.7$	-33.1 <sup>a</sup>
	$\langle y^2 \rangle = 0$	3.5	3.9	$\chi_{\perp}^d = -73.4$	-75.9
HOCl	$\langle x^2 \rangle = 17.4$	21.1	21.3 ± 0.5 <sup>b</sup>	$\chi_{xx}^d = -34.8$	-36.9 <sup>b</sup>
	$\langle y^2 \rangle = 0.8$	4.5	4.8 ± 0.5	$\chi_{yy}^d = -105.2$	-106.9
	$\langle z^2 \rangle = 0$	3.7	3.9 ± 0.3	$\chi_{zz}^d = -108.6$	-110.7
	$\langle x^2 \rangle = 0.86$	4.3	4.48 <sup>c</sup>	$\chi_{xx}^d = -155.7$	-161.13 <sup>c</sup>
	$\langle y^2 \rangle = 1.03$	4.4	4.80	$\chi_{yy}^d = -155.3$	-159.77
	$\langle z^2 \rangle = 28.94$	32.3	33.18	$\chi_{zz}^d = -36.9$	-39.37
	$\langle x^2 \rangle = 0.82$	4.2	4.43 <sup>c</sup>	$\chi_{xx}^d = -158.2$	-161.30 <sup>c</sup>
	$\langle y^2 \rangle = 0.82$	4.2	4.43	$\chi_{yy}^d = -158.2$	-161.30
	$\langle z^2 \rangle = 29.65$	33.1	33.59	$\chi_{zz}^d = -35.6$	-37.59

	$\langle x^2 \rangle = 0.25$ $\langle y^2 \rangle = 1.69$ $\langle z^2 \rangle = 27.84$	3.65 5.1 31.2	4.15° 4.78 31.90	$d_{xx} = -154.0$ $d_{yy} = -147.8$ $d_{zz} = -37.1$	-156.00° -152.94 -38.27
	$\langle x^2 \rangle = 34.8$ $\langle y^2 \rangle = 9.9$ $\langle z^2 \rangle = 0$	39.6 14.7 4.8	40.2 <sup>d</sup> 14.2 5.1	$d_{xx} = -82.7$ $d_{yy} = -188.4$ $d_{zz} = -230.4$	-82.3 <sup>d</sup> -192.3 -231.3
	$\langle x^2 \rangle = 96.4$ $\langle y^2 \rangle = 51.4$ $\langle z^2 \rangle = 0$	104.2 59.2 7.8	105.4 ± 3.8° 57.9 ± 3.8 8.4 ± 3.8	$d_{xx} = -284.2$ $d_{yy} = -475.1$ $d_{zz} = -693.2$	-281.4 ± 8.8° -483.0 ± 10.0 -692.9 ± 10.7
	$\langle x^2 \rangle = 94.5$ $\langle y^2 \rangle = 51.7$ $\langle z^2 \rangle = 0$	102.3 59.5 7.8	103.2 ± 5.4° 59.1 ± 5.4 8.2 ± 5.4	$d_{xx} = -285.5$ $d_{yy} = -467.1$ $d_{zz} = -686.4$	-285.5 ± 11.7° -473.0 ± 14.0 -688.8 ± 14.6
	$\langle x^2 \rangle = 85.6$ $\langle y^2 \rangle = 33.1$ $\langle z^2 \rangle = 1.6$	92.8 40.3 8.8	90.8 ± 3.4 <sup>f</sup> 39.7 ± 3.4 9.1 ± 3.4	$d_{xx} = -208.3$ $d_{yy} = -431.0$ $d_{zz} = -564.7$	-207.3 ± 7.6 <sup>f</sup> -424.0 ± 10.2 -554.1 ± 10.6
	$\langle x^2 \rangle = 119.5$ $\langle y^2 \rangle = 83.2$ $\langle z^2 \rangle = 0$	128.3 92.0 8.8	129.0 ± 4.6° 91.2 ± 4.6 9.5 ± 4.6	$d_{xx} = -427.6$ $d_{yy} = -581.6$ $d_{zz} = -934.6$	-427.4 ± 11.5° -587.7 ± 11.3 -932 ± 12.2

Molecule	Second Moments			Diamagnetic Susceptibilities	
	Point charge approxn.	Additivity formula	Ab initio or exptl.	Additivity formula	Ab initio or exptl.
	$\langle x^2 \rangle = 40.5$ $\langle y^2 \rangle = 55.8$ $\langle z^2 \rangle = 2.5$	48.6	48.55 <sup>h</sup>	$\chi_{xx}^d = -316.1$ $\chi_{yy}^d = -251.2$ $\chi_{zz}^d = -477.3$	-320.22 <sup>h</sup> -255.66 -476.50
	$\langle x^2 \rangle = 59.7$ $\langle y^2 \rangle = 79.3$ $\langle z^2 \rangle = 0$	68.2 87.8 8.5	67.5 <sup>h</sup> 87.4 9.88	$\chi_{xx}^d = -408.5$ $\chi_{yy}^d = -325.4$ $\chi_{zz}^d = -661.8$	-412.80 <sup>h</sup> -328.26 -657.24
	$\langle x^2 \rangle = 30.22$ $\langle y^2 \rangle = 29.57$ $\langle z^2 \rangle = 0$	35.8 35.2 5.6	36.0 ± 0.4 <sup>l</sup> 34.9 ± 0.5 6.2 ± 0.4	$\chi_{xx}^d = -173.1$ $\chi_{yy}^d = -175.6$ $\chi_{zz}^d = -301.2$	-174.4 ± 1.1 <sup>l</sup> -178.8 ± 1.2 -300.8 ± 1.5
	$\langle x^2 \rangle = 50.67$ $\langle y^2 \rangle = 44.02$ $\langle z^2 \rangle = 0$	57.5 50.8 6.8	54.4 <sup>j</sup> 53.0 8.4	$\chi_{xx}^d = -244.4$ $\chi_{yy}^d = -272.8$ $\chi_{zz}^d = -459.5$	-260.3 -266.4 -455.5
F-Xe-F	$\langle z^2 \rangle = 72$ $\langle x^2 \rangle = \langle y^2 \rangle = 0$	79.6 7.6	83.59 <sup>k</sup> 7.37	$\chi_{  }^d = -64.5$ $\chi_{\perp}^d = -369.9$	-62.53 <sup>k</sup> -385.89

$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{Xe}-\text{F} \\   \\ \text{F} \end{array}$	$\langle x^2 \rangle = 68.4$	77.9	81.17 <sup>k</sup>	$\chi_{xx}^d = -370.8$	-381.82 <sup>k</sup>
	$\langle y^2 \rangle = 68.4$	77.9	81.17	$\chi_{yy}^d = -370.8$	-381.82
	$\langle z^2 \rangle = 0$	9.5	8.83	$\chi_{zz}^d = -661.0$	-688.71
XeF <sub>6</sub>	$\langle x^2 \rangle = 64.3$	75.8	78.25 <sup>k</sup>	$\chi_{xx}^d = -643.1$	-663.94 <sup>k</sup>
	$\langle y^2 \rangle = 64.3$	75.8	78.25	$\chi_{yy}^d = -643.1$	-663.94
	$\langle z^2 \rangle = 64.3$	75.8	78.25	$\chi_{zz}^d = -643.1$	-663.94
S=C=S	$\langle z^2 \rangle = 77.3$	83.3	83.2 <sup>l</sup>	$\chi_{  }^d = -50.9$	-50.9 <sup>l</sup>
	$\langle x^2 \rangle = 0$	6.0	6.0	$\chi_{\perp}^d = -353.4$	-353.0

\* The second moments and diamagnetic susceptibilities are expressed in units  $10^{-16}$  cm<sup>2</sup> and  $10^6$  cm<sup>3</sup> mole<sup>-1</sup> respectively.

<sup>a</sup> E. F. Pearson, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, **60** (1974) 1761.

<sup>b</sup> M. Suzuki and A. Guarnieri, *Z. Naturforsch.*, **30a** (1975) 497.

<sup>c</sup> B. T. Hart, *Aust. J. Chem.*, **26** (1973) 461.

<sup>d</sup> R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Amer. Chem. Soc.*, **95** (1973) 2772.

<sup>e</sup> C. L. Norris, R. S. Benson, P. Beak, and W. H. Flygare, *J. Amer. Chem. Soc.*, **95** (1973) 2766.

<sup>f</sup> W. Czieslik, U. Anderson, and H. Dreizler, *Z. Naturforsch.*, **28a** (1973) 1906.

<sup>g</sup> D. H. Sutter, *Z. Naturforsch.*, **29a** (1974) 786.

<sup>h</sup> W. Van Niessen, G. M. F. Diecksen, and L. S. Cederbaum, *Chem. Phys.*, **10** (1975) 345.

<sup>i</sup> J. R. Davidson, A. K. Burnham, B. Siegel, P. Beak, and W. H. Flygare, *J. Amer. Chem. Soc.*, **96** (1974) 7394.

<sup>j</sup> T. K. Ha and C. T. O'Konski, *Int. J. Quant. Chem.*, **7** (1973) 609.

<sup>k</sup> H. Basch, J. W. Moskowitz, C. Hollister, and D. Hankins, *J. Chem. Phys.*, **55** (1971) 1922.

the same period of the system of elements<sup>5,6</sup>. The reason for this constancy of the term  $\sum_{\mu} P_{\mu\mu} \langle \Phi_{\mu} | a_A^2(\mu) | \Phi_{\mu} \rangle$  is as follows. The more electronegative atoms have larger populations  $P_{\mu\mu}$ . However, the larger electron attractive power means that the corresponding atomic orbitals  $\Phi_{\mu}$  are less diffuse, *i. e.* they are more concentrated around the nucleus A giving rise to the smaller values of the  $\langle \Phi_{\mu} | a_A^2(\mu) | \Phi_{\mu} \rangle$  integrals. These two opposite effects approximately cancel each other giving theoretical justification of the additivity rules. The empirical additivity constants<sup>5,6</sup>, denoted by  $k_p$ , are summarized in the following Table (in  $10^{-16} \text{ cm}^2$ ):

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

where the zeroth period ( $p = 0$ ) comprises hydrogen and helium. The empirical formula for the electronic second moment of charge has the form:

$$\langle x^2 \rangle = \sum_n Z_n a_n^2 + \sum_p n_p k_p \quad (3)$$

where  $n_p$  is the number of atoms in a molecule which belong to the  $p$ -th period of the Mendeleev system of elements. It is the aim of this paper to check the empirical formula (3) against some most recent experimental and *ab initio* results with particular emphasis on molecules involving heavy atoms like S, Cl, Si, P and Xe. The evidence for molecules containing heavy atoms was scarce due to the lack of either experimental or theoretical results. Since the second moments and the related diamagnetic susceptibilities  $\chi^d$  are highly insensitive to the quality of the molecular wave-functions<sup>7</sup>, the *ab initio* results (excluding minimum basis set calculations employing poor atomic orbitals) should be close to the experimental ones.

If the geometries of molecules are known, the empirical formula (3) yields the values of the second moments by the »back of the envelope« calculation. The results are given in Table I. They are in a good agreement with available experimental values and *ab initio* results providing further justification of the additivity formula (3). The discrepancies are found in xenon fluorides where the chemical bonds are expected to have very high ionic character. In that case our assumption about neutrality of atoms in a molecule does not hold. The point charge approximation term  $\sum_n Z_n x_n^2$  should be adjusted to include the effect of charge transfer between atoms. This is achieved by replacing  $Z_n$  by  $Z_n - Q_n$  where  $Q_n$  is the gross atomic charge. The modified formula reads then as follows:

$$\langle x^2 \rangle = \sum_n (Z_n - Q_n) x_n^2 + \sum_p n_p k_p \quad (4)$$

Bash *et al.*<sup>8</sup> found that the gross atomic charges on fluorine are  $-0.652$ ,  $-0.614$  and  $-0.576$  for  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  respectively. By using these values and the formula (4) one obtains improvement of the empirical second moments as shown in Table II. The validity of the *ab initio* gross atomic charges depends on the quality of basis set and the adequacy of the charge partitioning technique. Nevertheless, the modified empirical second moments

exhibit shift in the right direction. Similar calculations<sup>9</sup>, where the gross atomic charge was estimated by the electronegativity differences, gave encouraging results for highly polar molecules like SnO, PbO, GeO, TlF, CsF *etc.*<sup>9</sup> It is interesting to mention that our results for carbon disulfide are in excellent agreement with the *ab initio* results of Nitzsche and Christoffersen<sup>10</sup> who used their molecular fragments method. Our results confirm that previous

TABLE II

The empirical second moments and diamagnetic susceptibilities obtained by the formula (4) for xenon fluorides XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>

Molecule	Second Moments		Diamagnetic Susceptibilities	
	Empirical	<i>Ab initio</i>	Empirical	<i>Ab initio</i>
XeF <sub>2</sub>	$\langle x^2 \rangle = 7.6$	7.37	$\chi_{xx}^d = -391.9$	-385.89
	$\langle y^2 \rangle = 7.6$	7.37	$\chi_{yy}^d = -391.9$	-385.89
	$\langle z^2 \rangle = 84.8$	83.59	$\chi_{zz}^d = -64.5$	-62.53
XeF <sub>4</sub>	$\langle x^2 \rangle = 82.6$	81.17	$\chi_{xx}^d = -390.7$	-381.82
	$\langle y^2 \rangle = 82.6$	81.17	$\chi_{yy}^d = -390.7$	-381.82
	$\langle z^2 \rangle = 9.5$	8.83	$\chi_{zz}^d = -700.8$	-688.71
XeF <sub>6</sub>	$\langle x^2 \rangle = 79.9$	78.25	$\chi_{xx}^d = -677.9$	-663.94
	$\langle y^2 \rangle = 79.9$	78.25	$\chi_{yy}^d = -677.9$	-663.94
	$\langle z^2 \rangle = 79.9$	78.25	$\chi_{zz}^d = -677.9$	-663.94

*ab initio* calculations of Fischer and Kemmey<sup>11</sup>, who obtained for  $\langle z^2 \rangle = 7.05 \cdot 10^{-16} \text{ cm}^2$ , are in error by the order in magnitude. The results of Fischer and Kemmey for second moments  $\langle x^2 \rangle = \langle y^2 \rangle = 6.88$  and  $\langle z^2 \rangle = 7.05$  (in  $10^{-16} \text{ cm}^2$ ) imply that the distribution of the electronic charge in S=C=S is almost spherically symmetrical what is physically unacceptable.

## REFERENCES

1. W. H. Flygare and R. C. Benson, *Mol. Phys.* **20** (1971) 225 and the references cited therein.
2. L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties*, Wiley, New York, 1972.
3. R. P. Blickensderfer, Y. H. S. Wang, and W. H. Flygare, *J. Chem. Phys.* **51** (1969) 3196.
4. J. E. Bloor and Z. B. Maksić, *Mol. Phys.* **22** (1971) 351.
5. Z. B. Maksić and J. E. Bloor, *Chem. Phys. Lett.* **13** (1972) 571; Z. B. Maksić and J. E. Bloor, *J. Phys. Chem.* **77** (1973) 1520.
6. Z. B. Maksić, *J. Mol. Structure* **20** (1974) 41.
7. J. E. Bloor and Z. B. Maksić, *Mol. Phys.* **26** (1973) 397.
8. H. Basch, J. W. Moskowicz, C. Hollister, and D. Hankins, *J. Chem. Phys.* **55** (1971) 1922.

9. Z. B. Maksić and N. Mikac (to be published).  
10. L. E. Nitzsche and R. E. Christoffersen, *J. Amer. Chem. Soc.* **96** (1974) 5989.  
11. C. R. Fischer and P. J. Kemmey, *Mol. Phys.* **22** (1971) 1133.

### SAŽETAK

#### Empirijsko računanje dijamagnetske susceptibilnosti molekula

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Primijenjene su originalne aditivne formule za izračunavanje drugih momenata raspodjele elektronskog naboja i dijamagnetske susceptibilnosti molekula koje sadrže atome S, Cl, Si, P i Xe. Izračunane vrijednosti su u dobrom slaganju s eksperimentalnim i *ab initio* rezultatima. Razmatran je utjecaj intramolekularnog prijenosa naboja na veličinu drugih momenata raspodjele.

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