

Semiempirical versus *ab Initio* Calculations of Molecular Properties. I. Diamagnetic Susceptibilities and Quadrupole Moments in Some Medium Size Molecules

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The self-consistent charge molecular orbital (SCC-MO) method was applied to a number of medium size molecules involving atoms exhibiting large differences in electronegativity and possessing one or more lone pairs. The quality of the wave functions thus obtained was applied to a number of medium size molecules involving atoms calculated by a rigorous treatment of the operators x^2 , y^2 , and z^2 . The SCC quadrupole moments can be favourably compared with the *ab initio* results of Snyder and Basch obtained by the use of a Gaussian double zeta basis set. The present results provide additional justification of the SCC method, which has apparent advantages over the methods based on the ZDO approximation. Some difficulties encountered in the treatment of pi-electrons are discussed and suggestions for their remedy are given. The second moments calculated by the application of a simple additivity formula (Z. B. Maksić and J. E. Bloor, *Chem. Phys. Lett.*, **13** (1972) 571; *J. Phys. Chem.*, **77** (1973) 1520) and the related diamagnetic susceptibilities are in very good agreement with the *ab initio* values.

INTRODUCTION

The distribution of the electronic charge in a molecule is intimately related to its physical and chemical properties such as spatial arrangement of nuclei, chemical reactivity etc. Since *ab initio* calculations are expensive and still not feasible for large molecules of chemical and biological interest, it is desirable to develop a reliable semiempirical method. In the latter, the rigorous calculation of Hartree-Fock matrix elements is replaced by their approximate treatment in order to gain efficiency. It is, therefore, necessary to develop sensitive tests for the quality of semiempirical molecular wave functions. The overall energy of a molecule is not such a good criterion because it is insensitive to the finer details of the charge density.¹ This drawback is particularly pronounced in large compounds where the total energy is essentially a sum of a large number of atomic energy terms, and the binding energy is consequently a small fraction of the overall molecular energy (1% or smaller). Very useful and sensitive probes of the electronic charge density in a particular region of a molecule are given by one-electron properties (such as dipole and quadrupole moments, elec-

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tric field gradients at the site of nuclei, Hellman-Feynman forces etc.), because they are sensitive to any first-order change of the molecular wave function². Owing to the variation theorem, the total energy is not affected to a first approximation. In the course of our study of one-electron properties,^{3,4} we have calculated molecular second moments, diamagnetic susceptibilities and molecular quadrupole moments for some medium size compounds by using self-consistent charge molecular orbitals (SCC-MO). The results are reported here and compared with available ab initio calculations performed by the same modest but flexible Gaussian basis sets with two contracted Gaussian functions per atomic orbital⁵. The use of a fixed basis set for various molecules is advantageous, because the inadequacies of the calculated wave functions are approximately constant and the errors tend to cancel when the properties of related molecules are compared. It seems that the quality of the Snyder and Basch results lies between the best-atom double zeta and the best-molecule double zeta ab initio calculations, as revealed by the comparison of the results for carbon monoxide⁵. The molecules considered in this paper are widely different and involve several heteroatoms in various bonding situations. The constituent atoms are considerably different in their electronegativities, thus providing critical tests for SCC-MO wave functions. The matrix elements of the operators x^2 , y^2 and z^2 over atomic orbitals were calculated rigorously by the method outlined earlier⁶, where integrals of the type $\langle \Phi_k | x^2 | \Phi_l \rangle$ were developed in series of overlap integrals. Since these integrals are computed exactly, the comparison of the afore-mentioned properties with ab initio results gives some insight into the quality of semiempirical SCC molecular orbitals. The discrepancies between the SCC and ab initio results will indicate shortcomings of the semiempirical approach and may perhaps suggest their remedy. The geometries of the molecules as well as the origin and orientation of the coordinate axes were taken from ref 5 in order to facilitate comparison. The main features of the SCC-MO method were discussed elsewhere³.

RESULTS AND DISCUSSION

Formal Atomic Charges and Overlap Populations

The partition of the total electronic charge among atoms and chemical bonds is quite arbitrary. Nevertheless, the derived quantities proved very useful in discussing physical and chemical properties of molecules, e. g. bond energies, proton chemical shifts, inner-core binding energy shifts etc. It is, therefore, interesting to compare SCC-MO effective charges of atoms and overlap populations with the corresponding ab initio quantities. We shall follow Mulliken's definitions⁷ of these quantities because they are built-in into the SCC-MO method and were also used by Snyder and Basch. It should be mentioned that several other definitions were suggested⁸⁻¹². In any case, Mulliken's convention is the simplest and most commonly used one in the literature. The total number of electrons, n , in a closed-shell molecule can be written as a sum

$$n = 2 \sum_{i=1}^{\text{occ.}} \int \Psi_i^2 dv \quad (1)$$

owing to the normalization condition of molecular orbitals ψ_i ($i = 1 \dots n/2$) which are linear combinations of atomic orbitals,

$$\Psi_i = \sum_{\mu} c_{i\mu} \Phi_{\mu} \quad (2)$$

Substituting (2) into (1) one obtains

$$n = \sum_{\mu} P_{\mu\mu} + 2 \sum_{\mu < \nu} P_{\mu\nu} S_{\mu\nu} \quad (3)$$

where the quantities $P_{\mu\nu}$ are the well known elements of the bond-order charge-density matrix and $S_{\mu\nu} = \int \Phi_{\mu} \Phi_{\nu} dv$ is the overlap integral between the atomic orbitals Φ_{μ} and Φ_{ν} . Since the way of summation is arbitrary, we may express the total electronic charge as a sum of atomic and interatomic contributions*:

$$n = \sum_{\mu} \sum_{\mu \in A} P_{\mu\mu} + 2 \sum_{A < B} \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu} \quad (4)$$

In the Mulliken population analysis, the portion of the electronic charge, $2 \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu}$, belonging to a pair of atoms A and B is equally divided between the constituent atoms. Thus, we have

$$n = \sum_{\mu \in A} P_{\mu\mu} + \sum_{B \neq A} \left[\sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu} \right] = \sum_{\mu \in A} n_{A\mu} \quad (5)$$

The expression within the outer parentheses is called the *total gross population* of the atom A, and it is a sum of the total gross populations of atomic orbitals Φ_{μ} centered on the nucleus A,

$$n_A = \sum_{\mu \in A} n_{A\mu} \quad (6)$$

where

$$n_{A\mu} = P_{\mu\mu} + \sum_{B \neq A} \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu} \quad (7)$$

Finally, the effective charge of an atom A in a molecule is given by

$$q_A = Z_A - n_A \quad (8)$$

where Z_A is the atomic number and n_A is the total gross population defined by equation 6. The interpair electronic charge density

$$n_{AB} = 2 \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu} \quad (9)$$

is termed *overlap population* and it is closely related to bonding and nonbonding (or repulsive) interactions in a molecule. If A and B are directly bonded atoms, then n_{AB} is a relatively large positive quantity which provides a good measure of the bonding strength^{1,13,14}. The overlap population n_{AB} is a sum of subtotal overlap populations between the basis functions Φ_{μ} and Φ_{ν} residing on the nuclei A and B, respectively:

$$n_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} n_{AB}(\mu, \nu) \quad (10)$$

* It is tacitly assumed here that orbitals placed on the same nucleus are mutually orthogonal. This is completely justified because inner-shell 1s electrons are excluded in the SCC-MO treatment.

where

$$n_{AB}(\mu, \nu) = 2 P_{\mu\nu} S_{\mu\nu} \quad (11)$$

Both n_{AB} and $n_{AB}(\mu, \nu)$ are intimately related to the hybridization of atomic orbitals¹⁵. The SCC-MO effective charges of atoms and overlap populations are compared with ab initio values in Table I. Some caution is needed here for several reasons. Firstly, all valence-electron semiempirical charge densities are not, strictly speaking, comparable with ab initio ones, because core-electrons are not explicitly considered in the former approach. We will assume that, to a good approximation, the 1s electrons form highly localized, impenetrable and unpolarizable cores which diminish the respective nuclear positive charge by two units. Furthermore, the Gaussian double zeta atomic basis set of Snyder and Basch employs only s- and p-type functions but it does not include the polarization d-functions. Therefore, the polarization of the atomic charge distribution by the Coulombic environment may not be very well represented. It was observed that the basis set used tends to force a more spherical charge distribution around the nucleus as compared with the more refined extended basis set calculations⁵. In addition, the electropositive property of hydrogen atoms is probably not well described by the Snyder and Basch calculations, because their formal charges seem to be somewhat exaggerated. In spite of apparent deficiencies of both approaches, certain conclusions may be drawn from the data presented in Table I. The formal atomic charges for SCC-MO densities are smaller in absolute values than the corresponding entities for ab initio wave functions. Since the EHT method grossly overestimates the intramolecular charge transfer, it seems that the iterative variation of the method shows considerable changes in a proper direction. Serious discrepancies (wrong sign) were found mainly for conjugated carbon atoms, e.g. C₁ in carbon suboxide and acrolein indicating that the use of an anisotropic set of atomic functions in the SCC method would be highly desirable. The overlap populations are systematically smaller for ab initio charge-density distributions, which is probably a consequence of the lack of polarization functions in the basis sets. The overlap populations for different chemical bonds should not be compared, because they are influenced by the different nuclear cores. However, if a specific bond is considered in different chemical environments, the overlap population is a good index for the bonding type and bonding strength. For example, the overlap population for the C—C bond in ethylene oxide, 0.632, is considerably smaller than the corresponding value in ethane, thus reflecting the angular strain inherent in the small three-membered ring. The overlap populations for C=C double bonds in carbon suboxide and acrolein are 1.405 and 1.232, respectively, indicating the difference in hybridization of sigma orbitals which can be crudely characterized by sp and sp² canonical states. Summarizing our considerations, we may say that the agreement between SCC and ab initio molecular wave functions of Snyder and Basch is more qualitative than quantitative as far as the population analysis is concerned. Comparison of SCC charge densities with more ambitious ab initio calculations is desirable. One should try to improve the SCC wave function by fitting the ab-initio charge distribution (and multipole moments) for characteristic compounds employing anisotropic basis sets, local hybrid orbitals and better parametrization. Furthermore, Mulliken's equipartition of overlap charges is apparently an oversimplification when atoms with significantly different electronegativities

TABLE I

Comparison Between the SCC-MO and *ab Initio* Charge Distributions in Some Small Polyatomic Molecules

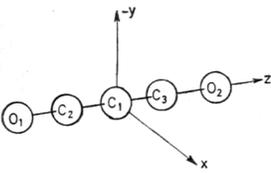
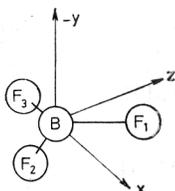
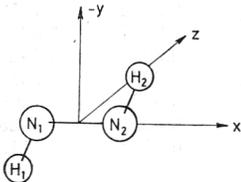
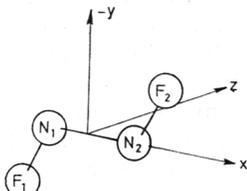
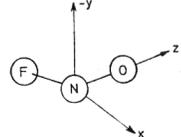
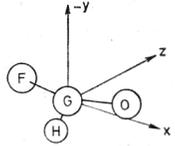
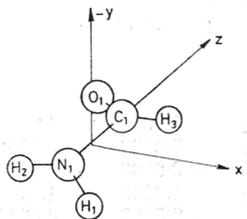
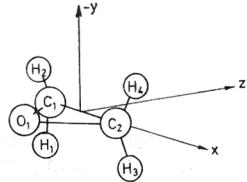
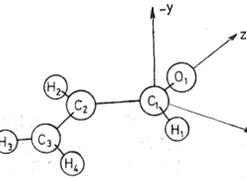
Molecule	Effective atomic charges		Overlap populations			
	SCC-MO	<i>ab initio</i>	SCC-MO	<i>ab initio</i>		
	C ₁	0.088	-0.7109	C ₁ -C ₂	1.4054	1.0915
	C ₂	0.221	0.6179	C ₂ -C ₃	-0.0739	0.0802
	O ₁	-0.265	-0.2624	C ₁ -O ₁	-0.0706	-0.0063
				C ₂ -O ₁	1.2442	1.1728
				C ₃ -O ₁	-0.0003	0.0010
				O ₁ -O ₂	0	0
	B	0.682	0.8193	B-F ₁	0.7590	0.6373
	F	-0.227	-0.2731	F ₁ -F ₂	-0.0155	-0.0807
	N	-0.095	-0.2949	N ₁ -H ₁	0.7496	0.6423
	H	0.095	0.2949	N ₁ -H ₂	-0.1203	-0.1596
				N ₁ -N ₂	1.1057	0.5988
				H ₁ -H ₂	-0.0298	0.0134
	N	0.194	0.253	N ₁ -N ₂	1.1591	0.5061
	F	-0.194	-0.253	N ₁ -F ₁	0.4546	0.1480
				N ₁ -F ₂	-0.0516	-0.1350
				F ₁ -F ₂	0.0002	0.0064
	N	0.259	0.4591	O ₁ -N ₁	1.2182	0.6363
	O	-0.031	-0.0708	F ₁ -N ₁	0.3147	0.0702
	F	-0.228	-0.3888	F ₁ -O ₁	-0.0455	-0.1675
	O	-0.228	-0.3047	C ₁ -H ₁	0.7871	0.7685
	F	-0.256	-0.2780	O ₁ -H ₁	-0.0571	-0.0877
	C	0.377	0.3787	O ₁ -C ₁	1.2190	1.1805
	H	0.107	0.2041	F ₁ -H ₁	-0.0467	-0.1088
				F ₁ -C ₁	0.5849	0.3456

Table I. (contd.)₁

Molecule	Effective atomic charges		Overlap populations			
	SCC-MO	ab initio	SCC-MO		ab initio	
	N	-0.046	-0.7585	H ₁ -H ₂	-0.0703	-0.0349
	O	-0.409	-0.3775	H ₁ -H ₃	-0.0126	0.0065
	C	0.187	0.2576	C ₁ -H ₃	0.7874	0.7734
	H ₁	0.104	0.3577	N ₁ -H ₁	0.7405	0.6264
	H ₂	0.107	0.369	N ₁ -H ₂	0.7549	0.6476
	H ₃	0.057	0.1518	C ₁ -N ₁	0.889	0.4957
				N ₁ -H ₃	-0.0673	-0.1680
	O	-0.429	-0.4469	H ₁ -H ₂	-0.0567	-0.0467
	C ₁	0.119	-0.1456	C ₁ -H ₁	0.8128	0.7587
	H ₁	0.048	0.1846	C ₁ -C ₂	0.6322	0.4277
				O ₁ -C ₁	0.5147	0.2380
	O	-0.380	-0.3521	C ₁ -H ₁	0.7904	0.7571
	C ₁	0.147	0.1260	C ₁ -O ₁	1.0511	1.1217
	C ₂	0.049	-0.1275	C ₁ -C ₂	0.9222	0.6444
	C ₃	0.041	-0.4054	C ₂ -H ₂	0.8044	0.7812
	H ₁	0.048	0.1374	C ₂ -C ₃	1.2317	1.0082
	H ₂	0.033	0.2320	C ₃ -H ₃	0.8058	0.7428
	H ₃	0.031	0.2046	C ₃ -H ₄	0.8085	0.8014
	H ₄	0.032	0.1850	O ₁ -H ₁	-0.0606	-0.1309
				O ₁ -H ₂	-0.0051	0.0023
				O ₁ -C ₂	-0.0713	-0.1112

are involved. Since the iterative procedure leans heavily on the gross orbital populations, one should carefully examine other formal divisions of the overlap charge densities. At the very end of this section, it should be pointed out that the SCC effective charges of atoms were successfully correlated with inner-core binding energy shifts for a large variety of molecules involving first row atoms^{16,17}. The results are by far superior to the CNDO/2 approach. Thus, the SCC-MO charge distributions (at least if properly scaled) provide a fair account of the electronic migration in molecules.

Second Moments and Diamagnetic Susceptibilities

The second moment of the electronic charge distribution is defined by

$$\langle r_\alpha^2 \rangle = \langle 0 | \sum_i r_{\alpha i}^2 | 0 \rangle \quad (12)$$

where α stands for x, y and z, \mathbf{r} is the position vector measured from the origin of the space-fixed coordinate system of axes, the sum over i is extended over all electrons in a molecule and $\langle 0 | | 0 \rangle$ denotes the average value over the ground state antisymmetrized wave function*. It provides rough infor-

* The proper definition of the second moment should include a factor $-|e|$, but we shall drop it for the sake of simplicity.

mation about the outer shape of the electronic cloud. The second moments are intimately related to the diagonal elements of the diamagnetic susceptibility tensor¹⁸,

$$\chi_{\alpha\alpha}^d = \frac{-Ne^2}{4mc^2} \langle 0 | r_\beta^2 + r_\gamma^2 | 0 \rangle \quad (13)$$

where N is the Avogadro number, and the other physical constants have their usual meaning. The Greek subscripts may be any of the Cartesian components x , y and z in cyclic order. Comparison of SCC second moments with the Snyder-Basch *ab initio* results shows that the two sets of data are in a good agreement (Table II). The striking feature of the results is that the SCC second moments are systematically too low in the direction perpendicular to the principal symmetry axis of linear molecules or perpendicular to the plane of the heavy atoms of planar or approximately planar molecules. This is consistent with our earlier findings³, indicating that pi-electrons are bound too tightly in the SCC method. This inadequacy can be easily removed by the use of larger screening constants for pi-electron atomic orbitals, i. e. by exploiting anisotropic basis sets. The diamagnetic contributions to the molecular susceptibilities are also in good agreement with the *ab initio* values (Table II). This is, however, less a consequence of the good quality of the SCC wave functions than a result of the high insensitivity of the diamagnetic susceptibility and the second moments of the electronic charge distribution. In fact, we have shown in a series of papers that the latter quantities are easily calculated by simple additivity formulas¹⁹⁻²¹. The second moment (eq 12) can be broken down into three terms:

$$\begin{aligned} \langle r_\alpha^2 \rangle = & \sum_A \sum_\mu P_{\mu\mu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\mu \rangle + 2 \sum_{\mu < \nu} \sum_A \sum_A P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle + \\ & + 2 \sum_{A < B} \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle \quad (\alpha = x, y, z) \end{aligned} \quad (14)$$

The first two terms are atomic contributions, whereas the third term is related to chemical bonds. Expression 14 can be simplified by a series of approximations which were thoroughly discussed elsewhere¹⁹⁻²¹. The final formula reads as follows:

$$\langle r_\alpha^2 \rangle \cong \sum_A Z_A r_{\alpha A}^2 + \sum_p n_p k_p \quad (15)$$

where the α -th coordinate of atom A is denoted by $r_{\alpha A}$ and n_p is the number of atoms in a molecule which belong to the p -th period of the Mendeleev system of elements. The corresponding correction constant is assigned by k_p . This constant is isotropic because it does not depend on α . It is tacitly assumed here that the intramolecular charge transfer can be neglected in a first approximation. It should be taken into account only for molecules exhibiting high ionic character, e. g. alkali halides. The additivity formula 15 yields the second moments and diagonal elements of the diamagnetic susceptibility tensor in very good accordance with the *ab initio* values (Table II). The present results show once again that these two quantities cannot serve as aids in the quantum mechanical appraisal of the molecular wave functions. They, however, provide a useful test of the employed *basis set*, for if the *ab initio* values deviate from the experimental data, the basis set is of poor quality and should be discarded.

TABLE II
 Comparison Between the Semiempirical and *ab Initio* Second Moments and
 Diamagnetic Susceptibilities for Some Medium Size Molecules

Molecule	Second Moments ^a			<i>ab initio</i>	Diamagnetic Susceptibilities ^b			
	Additivity formula	SCC-method ^c			Additivity formula	SCC-method	<i>ab initio</i>	
C ₃ O ₂	$\langle x^2 \rangle =$	5.0	4.95	5.52	$\chi_{xx}^d =$	6.032	6.034	6.056
	$\langle y^2 \rangle =$	5.0	4.95	5.52	$\chi_{yy}^d =$	6.032	6.034	6.056
	$\langle z^2 \rangle =$	119.9	123.16	123.06	$\chi_{zz}^d =$	5.520	0.466	0.520
BF ₃	$\langle x^2 \rangle =$	26.6	26.85	27.58	$\chi_{xx}^d =$	1.443	1.413	1.473
	$\langle y^2 \rangle =$	4.0	3.17	3.71	$\chi_{yy}^d =$	2.509	2.529	2.598
	$\langle z^2 \rangle =$	26.6	26.85	27.58	$\chi_{zz}^d =$	1.443	1.413	1.473
N ₂ H ₂	$\langle x^2 \rangle =$	9.7	9.25	10.02	$\chi_{xx}^d =$	0.309	0.255	0.308
	$\langle y^2 \rangle =$	4.2	3.36	3.99	$\chi_{yy}^d =$	0.571	0.532	0.592
	$\langle z^2 \rangle =$	2.4	2.06	2.55	$\chi_{zz}^d =$	0.655	0.593	0.659
N ₂ F ₂	$\langle x^2 \rangle =$	26.9	27.19	27.67	$\chi_{xx}^d =$	1.911	1.906	1.867
	$\langle y^2 \rangle =$	36.6	37.12	35.57	$\chi_{yy}^d =$	1.454	1.438	1.495
	$\langle z^2 \rangle =$	4.0	3.34	4.07	$\chi_{zz}^d =$	2.989	3.029	2.979
FNO	$\langle x^2 \rangle =$	14.8	14.40	15.0	$\chi_{xx}^d =$	0.841	0.824	0.857
	$\langle y^2 \rangle =$	3.0	2.42	2.96	$\chi_{yy}^d =$	1.397	1.388	1.437
	$\langle z^2 \rangle =$	14.9	15.07	15.51	$\chi_{zz}^d =$	0.838	0.792	0.846
CHOF	$\langle x^2 \rangle =$	23.9	24.63	25.13	$\chi_{xx}^d =$	0.490	0.448	0.479
	$\langle y^2 \rangle =$	3.2	2.77	3.18	$\chi_{yy}^d =$	1.466	1.478	1.513
	$\langle z^2 \rangle =$	7.2	6.75	7.00	$\chi_{zz}^d =$	1.277	1.291	1.333
CHONH ₂	$\langle x^2 \rangle =$	11.9	11.76	11.77	$\chi_{xx}^d =$	1.370	1.355	1.377
	$\langle y^2 \rangle =$	3.7	3.53	4.01	$\chi_{yy}^d =$	1.748	1.742	1.748
	$\langle z^2 \rangle =$	25.4	25.23	25.35	$\chi_{zz}^d =$	0.743	0.720	0.743
C ₂ H ₄ O	$\langle x^2 \rangle =$	16.7	16.42	16.21	$\chi_{xx}^d =$	0.941	0.958	0.963
	$\langle y^2 \rangle =$	7.2	7.01	6.96	$\chi_{yy}^d =$	1.387	1.401	1.399
	$\langle z^2 \rangle =$	12.8	13.33	13.49	$\chi_{zz}^d =$	1.123	1.104	1.091
C ₃ H ₄ O	$\langle x^2 \rangle =$	21.3	21.08	20.88	$\chi_{xx}^d =$	2.899	2.951	2.975
	$\langle y^2 \rangle =$	4.8	4.82	5.36	$\chi_{yy}^d =$	3.673	3.717	3.706
	$\langle z^2 \rangle =$	56.7	57.83	57.80	$\chi_{zz}^d =$	1.227	1.220	1.236

^a In 10⁻²⁰ m units.

^b In 10⁻¹² m³/mol units.

Concomitantly, the operators r_α^2 ($\alpha = x, y, z$) and their combinations are not useful in the constrained variational calculations of molecular wave functions. Actual studies of Whitehead and Zeiss have shown that they are really not very effective²⁴.

Molecular Quadrupole Moments

The electric quadrupole moment is a tensor of second rank. It is defined by means of second moments in such a way that it is symmetrical and traceless:

$$Q_{\alpha\beta} = 1/2 \left| e \left| \sum_A Z_A (3r_{\alpha A} r_{\beta A} - r_A^2 \delta_{\alpha\beta}) - 1/2 \left| e \right| \langle 0 \left| 3r_\alpha r_\beta - r^2 \delta_{\alpha\beta} \right| 0 \right. \right. \right. \quad (16)$$

For a particular choice of α and β ($\alpha = \beta = x$), $Q_{\alpha\beta}$ takes the form

$$Q_{xx} = 1/2 \left| e \left| \sum_A Z_A (3r_{xA}^2 - r_A^2) - 1/2 \left| e \right| \langle 0 \left| 3r_x^2 - r^2 \right| 0 \right. \right. \right. \quad (17)$$

We shall consider only the diagonal elements of the quadrupole moments. The relevance of the molecular quadrupole moments stems from the fact that they play an important role in the theory of intermolecular forces. It has been long realized that the detailed knowledge of molecular multipoles is essential for an understanding of interactions between systems with nonoverlapping charge clouds²⁵. They are, therefore, important for the theoretical treatment of interactions appearing in solids, liquids and molecular biology. Furthermore, electrostatic molecular potentials are a useful tool in studying certain chemical reactions. They reveal, at least qualitatively, the positions and channels for electrophilic reagents²⁶. Finally, quadrupole moments provide a very sensitive test for the precision of approximate wave functions, particularly in their regions at medium and large distance from nuclei. As mentioned before, these regions of electronic charge distributions are not necessarily well determined by energy minimization which is mostly affected by the electronic cloud in the immediate vicinity of nuclei. The SCC molecular quadrupole moments were calculated by treating the inner-shell 1s electrons in a point charge approximation. The SCC and ab initio molecular quadrupoles are compared in Table III. The semiempirical results are in good agreement with the ab initio ones. This is encouraging, because the molecular quadrupoles, unlike the second moments, are very sensitive to the atomic dipole term and the three-center term in expression 14, which involves the overlap populations. It should be strongly pointed out that the CNDO/2 method, which was designed to mimic ab initio dipole moments, is completely unsatisfactory for the prediction of molecular quadrupoles^{3,27}. This drawback could be overcome only by the symmetric deorthogonalization of the CNDO/MO's prior to the calculation of quadrupoles³. A slight improvement was also found for dipole moments²⁸ and electron density maps²⁹. Since the SCC method gives much better correlations with ESCA chemical shifts than the CNDO/2 method does, it seems that the SCC approach offers better perspectives than the methods based on the ZDO approximation. The origin of the high sensitivity of molecular quadrupoles to finer details of the charge distribution is apparent from formula 16, showing that the quantity represents itself as two large terms opposite in signs and comparable in magnitudes. This is not surprising, because the extent of charge reorganization accompanying the formation of a molecule

TABLE III
 Comparison Between the Semiempirical and *ab Initio* Molecular Quadrupole Moments
 (in 10^{-30} Cm²)

Molecule	Point charge	Point bond	SCC method	<i>ab initio</i>
C ₃ O ₂	Q _{xx} = 6.22	1.59	2.65	2.104
	Q _{yy} = 6.22	1.59	2.65	2.104
	Q _{zz} = -12.44	-3.18	-5.30	-4.208
BF ₃	Q _{xx} = -0.92	-0.98	-0.83	-0.987
	Q _{yy} = 1.84	1.96	1.66	1.974
	Q _{zz} = -0.92	-0.98	-0.83	-0.987
N ₂ H ₂	Q _{xx} = 0.12	0.69	-0.12	-0.148
	Q _{yy} = 0.35	0.54	0.64	0.640
	Q _{zz} = -0.47	-1.23	-0.52	-0.492
N ₂ F ₂	Q _{xx} = 0.38	1.15	-0.59	-0.420
	Q _{yy} = -1.87	-1.49	-1.14	-0.902
	Q _{zz} = 1.49	0.34	1.73	1.322
FNO	Q _{xx} = 1.33	-1.52	-0.16	-0.337
	Q _{yy} = -0.91	0.02	1.02	1.000
	Q _{zz} = -0.42	1.50	-0.86	-0.663
CHOF	Q _{xx} = -1.88	-1.11	-1.86	-2.128
	Q _{yy} = 1.04	-0.14	0.89	0.840
	Q _{zz} = 0.84	1.25	0.97	1.288
CHONH ₂	Q _{xx} = -0.16	1.11	-0.04	0.417
	Q _{yy} = 0.81	-0.25	-0.05	-0.718
	Q _{zz} = -0.65	-0.86	0.09	0.301
C ₂ H ₄ O	Q _{xx} = 2.16	1.57	0.66	1.083
	Q _{yy} = 0.86	1.47	0.54	0.581
	Q _{zz} = -3.02	-3.04	-1.20	-1.664
C ₃ H ₄ O	Q _{xx} = 1.25	0.06	1.00	1.745
	Q _{yy} = -0.94	2.93	0.78	-0.269
	Q _{zz} = -0.31	-2.99	-1.78	-1.476

from constituent atoms amounts only a small fraction of an electronic charge, e .³⁰ Keeping in mind that the molecular quadrupole moment is not an easily tractable quantity, we will try to apply two simple models for its calculation. The first is based on the gross atomic charges as calculated by the SCC method. Then the molecular quadrupole moment takes the form

$$Q_{xx} = 1/2 \left| e \sum_A (Z_A - n_A) (3r_{xA}^2 - r_A^2) \right| \quad (18)$$

where $(Z_A - n_A) = q_A$ is the effective charge of the atom A in a point charge approximation. The second method is based on an approach termed the point-

-bond model. In this method, the orbital overlap populations are arbitrarily placed at the midpoints of the corresponding chemical bonds while the orbital populations $P_{\mu\mu}$ of the atomic functions Φ_{μ} are placed at the respective nuclei. The results obtained by these two methods are also included in Table III, but they are highly erratic. The point-bond model is somewhat better than the point-charge model which gives the wrong sign for 9 out of 27 components. Thus, the limitations of the models are obvious and both approaches should be used with due care.

CONCLUSION

The molecules considered in this work involve atoms possessing one or more lone pairs. They differ widely in electronegativities, thus providing critical tests for any semiempirical method. One of them, the SCC method, was applied for the calculation of second moments, diamagnetic susceptibilities and molecular quadrupole moments. The results may be favourably compared with the available ab initio values. Since molecular quadrupoles are highly sensitive to the quality of the wave functions, the good agreement between the SCC and ab initio results indicates that the intramolecular charge transfer accompanying the formation of molecules is taken into account fairly well by the iterative self consistent charge procedure. This conclusion is concomitant with our earlier findings³. Some discrepancies were observed for second moments (and the related molecular quadrupoles and diamagnetic susceptibilities) which correspond to coordinate axes perpendicular to the principal symmetry axis of linear molecules or perpendicular to the molecular plane for planar systems. This is a consequence of the too tightly bound p-electrons in the SCC approach. This feature indicates that considerable improvement of the SCC wave functions might be obtained by the use of an anisotropic basis set. Furthermore, the replacement of the overlap density

$$\Phi_{\mu} \Phi_{\nu} = S_{\mu\nu} [w_{\mu} \Phi_{\mu}^2 + w_{\nu} \Phi_{\nu}^2] \quad (19)$$

by the weighted atomic orbital one-center densities, where $w_{\mu} + w_{\nu} = 1$, should be advantageous. Although the values of w_{μ} and w_{ν} do not deviate appreciably from 1/2 for π -electrons^{31,32}, uneven distribution of the mixed density $\Phi_{\mu} \Phi_{\nu}$ for σ -orbitals could be anticipated for atoms with considerably different sizes (and electronegativities). The partition of the $\Phi_{\mu} \Phi_{\nu}$ density, which preserves not only a barycentre of this distribution but also its higher moments was recommended by Čížek³³. Another approximate formula worth studying is that of Ruedenberg³⁴ in the weighted form:

$$\Phi_{\mu}^A \Phi_{\nu}^B = w_{\mu\nu}^A \sum_{\alpha=1}^A S_{\nu\alpha} \Phi_{\mu}^A \Phi_{\alpha}^A + w_{\mu\nu}^B \sum_{\beta=1}^B S_{\mu\beta} \Phi_{\beta}^B \Phi_{\nu}^B \quad (20)$$

All these possibilities should be thoroughly examined, because the definition of the atomic charge is of fundamental importance for the SCC-MO method. In fact, the diagonal elements of the secular equation are determined through valence shell ionization potentials which are functions of atomic charges. Thus, the definition of formal atomic charges is directly related to orbital energies. Since the valence orbital ionization potentials are influenced by neighbouring charges, the Madelung potential should also be included³⁵. Further semiempirical work along this line is highly desirable. To conclude, in spite of some imper-

fections, the SCC-MO method provides a good alternative to semiempirical methods based on the ZDO approximation, which encounter serious difficulties in predicting molecular quadrupole moments.

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SAŽETAK

Usporedba semiempirijskih i ab initio računa molekularnih svojstava. I. Dijamagnetska susceptibilnost i kvadrupolni momenti nekih molekula srednje veličine

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Primjenjena je semiempirijska metoda samousklađenog naboja na proučavanje niza molekula čiji se atomi znatno razlikuju po elektronegativnosti te posjeduju jedan ili više osamljenih parova elektrona. Kvaliteta dobivenih valnih funkcija provjerena je računanjem kvadrupolnih momenata i njihovom usporedbom s mnogo točnijim ab initio rezultatima. Postignuto slaganje govori u prilog primjenjenoj metodi koja ima niz prednosti pred semiempirijskim pristupima temeljenim na aproksimaciji »nultog diferencijalnog prekrivanja«. Izračunane dijamagnetske susceptibilnosti su u izvrsnom slaganju s ab initio vrijednostima. Ova veličina je, međutim, neosjetljiva o kvaliteti valnih funkcija pa se može dobiti i pomoću jednostavnih aditivnih formula, koje je razvio jedan od autora.

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