CCA-729

539.19:546.161
Original Scientific Paper

The Calculation of Molecular Quadrupole Moments in Some Fluorine Containing Compounds by the SCC Method*

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Received August 27, 1972

SCC (self-consistent charge) method was applied to a series of related fluorinated hydrocarbons. The calculated anisotropies of the second moments of the charge and the molecular quadrupoles are in fairly good agreement with experimental data. The results indicate that coulomb repulsion between electrons are absorbed satisfactorily into the parameterization of the SCC method.

INTRODUCTION

Inspite of the fact that the use of the Gaussian orbitals in molecular quantum mechanics has considerably increased the scope of high quality *ab initio* Hartree-Fock calculations, this procedure, because of computational complexities and computer costs, is still confined to rather small molecules. Therefore properties of molecules of medium and large size must still be explored by semiempirical methods. However, there are many different variations of semiempirical methods in the literature which are based on different theoretical models and sets of approximations so that there is a need for studies on a large variety of molecules in order to test the reliability of the different methods. The aim of this paper is twofold: *(a)* to examine the ability of one semiempirical method, namely the SCC (self-consistent charge) method, in predicting molecular quadrupole moments and related quantities, and *(b)* to discuss the electronic charge distribution obtained by the SCC method, since the molecular quadrupoles are very sensitive to the quality of the computed molecular wavefunctions. The latter is possible in particular because in our procedure,[1] the elements of the molecular quandrupole tensor are calculated accurately without further approximation. The technique we use for calculating the multicenter integrals is the Gaussian transform method.[2] By calculating the molecular property without further approximation we can now attribute any differences between the calculated and the experimental molecular quadrupoles as a measure of a »goodness« of the SCC molecular orbitals. The calculations we report here are for a series of fluorinated hydrocarbons: F_2CO, HCOF, H_2CF_2, $H_2C = CF_2$, HFC = CFH-*cis*, C_2H_3F, C_2H_5F and also for the related molecule formic acid HCOOH.

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* This work was supported in part by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1184-67, and through a UT Faculty Research Grant.

METHOD AND RESULTS

There are essentially two different approaches in use in semiempirical treatments today. The first employs the ZDO (zero differential overlap) approximation and consequently neglects all overlap integrals; however, coulomb repulsion integrals between electrons are taken into account explicity. The most commonly used example of this type of semiempirical method is the CNDO method and its variations.[3] The second group of semiempirical methods is characterised by inclusion of all overlap integrals in the secular equation, but the electronic repulsions are completely ignored. These methods are derived from the EH (Extended Hückel) method. However, it is well established by now that the EH method grossly overestimates electronic charge transfer in heteroatomic molecules and fails to give reliable results in many other respects.[3] It is better to use the SCC method which takes advantage of both semiempirical schemes, *i. e.*, it retains all overlap integrals and attempts to mimic electron repulsion effects by including a charge dependence of the Hamiltonian matrix elements.[4,5] Thus diagonal elements of the SCC Hamiltonian are given by

$$H_{ii} = H^0_{ii} - B_k q_k \tag{1}$$

where H_{ii} and H^0_{ii} are the coulomb integrals for charged and neutral atoms respectively and q_k is the charge on the k-th atom. The constants B_k depend on the nature of the atom k only and are tabulated in ref. 5. The H^0_{ii} values are determined from the valence state ionization potentials given by Hinze and Jaffe.[6] Off-diagonal elements H_{ij} are evaluated by using a Mulliken type approximation,

$$H_{ij} = (1/2)\, k S_{ij} (H_{ii} + H_{jj}) \tag{2}$$

where S_{ij} is the overlap integral $S_{ij} = \int \Phi_i \Phi_j \, dv$ between atomic functions Φ_i and Φ_j and $k = 1.75$.

According to Buckingham[7] the diagonal elements of the molecular quadrupole tensor are defined as

$$Q_{aa} = 1/2 \,|e|\, \sum_A Z_A (3a^2_A - r^2_A) - 1/2 \,|e|\, (3 < a^2 >_e - < r^2 >_e) \tag{3}$$

where Z_A is the atomic number of the nucleus A and $\langle a^2 \rangle_e = \langle \psi_0 | \sum_i^{el.} a^2_i \,| \psi_0 \rangle$ is the average value of the operator $\sum_i^{el.} a^2_i$ over the ground state wavefunction ψ_0. The other elements are easily obtained by permutation of the inertial coordinates a, b, and c. The quantity $\langle a^2 \rangle_e$ is called the second moment of charge and provides some information about the overall size of the electronic charge in the direction a, while the molecular quadrupole Q_{aa} reflects any deviation from the spherical symmetry of the molecule in the a direction. It should be mentioned at this point that the inner core $(1s)^2$ electrons are not included in the SCC method. Therefore, their contribution to molecular quadrupoles and second moments of charge has to be estimated by some model. We have assumed that $(1s)^2$ electrons form highly localized and unpolarized cores so that their contribution to the molecular quadrupoles is manifested in cancellation of two units of the nuclear charge. This is illustrated by the following analysis. Consider a system of nuclei with $Z_A = 2$ which contains only inner core $(1s)_A^2$ electrons. According to eq. (3) the molecular quadrupole component Q_{aa} of the system is

$$Q_{aa} = |e| [\sum_A (3a_A^2 - r_A^2) - (3 < 1s_A | a^2 | 1s_A > - < 1s_A | r^2 | 1s_A >)] \tag{4}$$

which becomes by simple rearrangement

$$Q_{aa} = |e| \sum_A [3 (a_A^2 - < 1s_A | a^2 | 1s_A >) - (r_A^2 - < 1s_A | r^2 | 1s_A >)] \tag{5}$$

By using a transformation of the coordinates $v = v_A + v'_A$ ($v = a, b, c$), where v'_A denotes coordinates of an electron measured from the nucleus A, and noticing that one center integrals of the type $< 1s_A | v'_A | 1s_A >$ are zero, expression (5) becomes

$$Q_{aa} = |e| \sum_A [< 1s_A | (r'_A)^2 | 1s_A > - 3 < 1s_A | (a'_A)^2 | 1s_A >] \tag{6}$$

since $1s_A$ orbitals are spherically symmetrical it follows that $<1s_A|(a')^2|1s_A> = 1/3 < 1s_A | (r'_A)^2 | 1s_A >$ and Q_{aa} identically vanishes. In other words, the $(1s)_A^2$ electrons diminish the nuclear charge by two units. The contribution of the $(1s)^2$ electrons to $< a^2 >_e$ and $< b^2 >_e$ where the a and b coordinates axes span the plane of the heavy atoms in a molecule, is calculated by a point charge approximation. On the other hand their contribution to the out of plane second moment $< c^2 >_e$ can be neglected. Namely it can be easily shown that the corresponding integrals are actually very small when calculated for Slater 1s orbitals. Thus

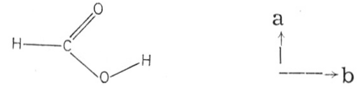
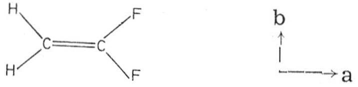
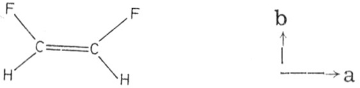
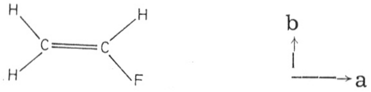
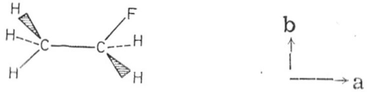
$$2 < 1s_A | c^2 | 1s_A > = 2 \left[\frac{a_0}{Z_A - S} \right]^2 \tag{7}$$

where a_0 is Bohr radius and S is a screening constant determined by Slater rules. By using the formula (7) we obtain the values 0.017, 0.012 and 0.01 (in 10^{-6} cm^2) for carbon, nitrogen and oxygen atoms, respectively. This is far beyond the accuracy of the SCC method.

Analysis of the molecular first and second order Zeeman effect in microwave spectra enables experimental determination of molecular quadrupoles and the anisotropies of the second moments of the charge distributions.[7] However, these values are somewhat ambiguous since the sign of the molecular g tensor cannot be determined experimentally. Therefore one obtains two sets of molecular quadrupole moments and a choice has to be made either by simple inspection and by comparison with similar molecules or by the application of the Flygare additivity rules for $< c^2 >_e$ values.[8] A comparison between the calculated anisotropies of second moments and molecular quadrupoles and experimental data is presented in Table I. Both sets of data reveal good agreement between theoretical and experimental values. Thus our results confirm earlier empirical assignments of the sing of the molecular g- tensor.[8–10] The only cases where both the choices of signs of the g-value give very similar anisotropies of the second moments and also molecular quadrupoles which are both close to the calculated entities are $CH_2 = CF_2$ and *cis*-$CHF = CHF$. However, even in these cases the choice of the negative g sign is more favo-

TABLE I

Comparison Between Experimental and Calculated Anisotropies in Second Moments of Charge Distribution and Molecular Quadrupoles

Molecule	Exp. (in 10^{-16} cm^2)	SCC	Exp. (in Buchinghams)	SCC
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 17.8 \pm 0.3$	17.97	$Q_{aa} = -5.3 \pm 0.6$	-6.69
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 22.1 \pm 0.3$	22.55	$Q_{bb} = 5.2 \pm 0.6$	4.81
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 4.3 \pm 0.3$	4.58	$Q_{cc} = 0.1 \pm 0.6$	1.87
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 4.6 \pm 0.1$	4.12	$Q_{aa} = 2.4 \pm 0.5$	2.79
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 27.2 \pm 0.2$	27.57	$Q_{bb} = -0.9 \pm 0.4$	-4.13
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 22.6 \pm 0.2$	23.45	$Q_{cc} = -1.5 \pm 0.8$	1.34
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 28.6 \pm 0.1$	29.44	$Q_{aa} = -1.7 \pm 0.4$	-4.75
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 42.2 \pm 0.1$	43.18	$Q_{bb} = 3.0 \pm 0.3$	3.43
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 13.6 \pm 0.1$	13.74	$Q_{cc} = 1.3 \pm 0.5$	1.46
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 1.3 \pm 0.1$	1.47	$Q_{aa} = -3.7 \pm 0.7$	-3.65
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 22.1 \pm 0.2$	22.34	$Q_{bb} = -0.2 \pm 0.5$	-1.40
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 20.8 \pm 0.2$	20.87	$Q_{cc} = 3.9 \pm 1.1$	5.05
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 16.8 \pm 0.1$	15.70	$Q_{aa} = -4.1 \pm 0.4$	-6.14
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 20.8 \pm 0.1$	18.96	$Q_{bb} = 1.9 \pm 0.3$	3.38
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 4.0 \pm 0.1$	3.27	$Q_{cc} = 2.2 \pm 0.6$	2.76
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 18.0$	18.30	$Q_{aa} = -4.5 \pm 0.2$	-5.79
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 21.8$	22.11	$Q_{bb} = 2.6 \pm 0.2$	3.12
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 3.8$	3.81	$Q_{cc} = 1.9 \pm 0.4$	2.67
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 20.7$	20.75	$Q_{aa} = -0.2 \pm 0.2$	-1.65
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 25.9$	26.46	$Q_{bb} = 3.1 \pm 0.2$	1.91
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 5.2$	5.70	$Q_{cc} = -2.9 \pm 0.3$	-0.27
	$\langle a^2\rangle_e - \langle b^2\rangle_e = 21.6$	21.79	$Q_{aa} = -2.0 \pm 0.4$	-3.9
	$\langle a^2\rangle_e - \langle c^2\rangle_e = 26.0$	26.26	$Q_{bb} = 1.3 \pm 0.4$	1.62
	$\langle b^2\rangle_e - \langle c^2\rangle_e = 4.4$	4.47	$Q_{cc} = 0.7 \pm 0.7$	1.47

rable. Analysis of the various contributions to the molecular quadrupoles was given in an earlier paper[1] and will not be repeated here. It was concluded that molecular quadrupoles depend mainly on anisotropies of the one center terms, including hybridization ones, and consequently these quantities reflect finer details of the electronic charge distribution. Despite the fact that molecular quadrupoles are so sensitive to the quality of the molecular orbitals, the calculated values obtained by the SCC method approach experimental ones quite closely. The exceptions are the out of plane Q_{cc} components of $CH_2 = CF_2$ and *cis*-CHF = CHF. Here the SCC method fails to predict a correct sign. This will be discussed later. The electronegativity effect is well reproduced by SCC method. For instance the oxygen atom and the fluorine atoms in HCOOH and CH_2F_2 respectively lie very near the inertial a axis and the corresponding Q_{aa} component is large and negative, due to a charge transfer towards the more electronegative atoms. In addition, calculated values parallel the experimental trend

$$|Q_{aa}|\, CH_2F_2 > |Q_{aa}|\, CHFCHF > |Q_{bb}|\, CH_2CF_2 > |Q_{bb}|\, OCF_2.$$

Analysis of the Zeeman effects in microwave spectra does not suffice for determination of individual second moments. One has to use in addition either bulk magnetic susceptibilities obtained by experiment (or by the use of Pascal additivity rules[11]) or the Flygare additivity rules for $< c^2 >_e$ second moments.[8] The latter were used by Flygare to obtain the experimental moments for all molecules except HCOOH which was the only molecule for which the experimental bulk magnetic susceptibility is known.[8-10] Experimental and calculated second moments are compared in Table II. The overall agreement with experiment is fairly good. One has to point out, however, that second moments are to a large extent insensitive to the molecular wavefunctions. We have found that in hydrocarbons very accurate estimates of the second moments are possible by using a simple generalization of the Flygare additivity rules.[12] The striking feature of the calculated second moments of charge is a too low value for the out of plane $< c^2 >_e$ component. It has been argued recently, on the basis of CNDO/2 calculations, that use of more diffuse π atomic orbitals would lead to better quadrupole moments.[13] Present results are in accordance with this idea. However, generally this is not the case and further evidence does not support this model of Meyer and Schweig.[14].

Since $< c^2 >_e$ second moments are too low the Q_{cc} molecular quadrupole component is generally too positive because the electronic contribution is proportional to $< r^2 >_e - 3 < c^2 >_e$. This is evident from Table I. Even more, if $< a^2 >_e$ and $< b^2 >_e$ second moments are determined very accurately then Q_{cc} values become so positive that the SCC method fails to predict the correct sign for this component of the molecular quadrupole tensor, as we found in the cases of $CH_2 = CF_2$ and HFC = CHF. It should be mentioned however that good agreement with experimental molecular quadrupoles does not necessarily mean that a good overall charge distribution has been achieved, but only that a good distribution is possible or even likely. $H\,CF_2$ provides an excellent illustrative example since all three second moments of charge are well below the experimental values while the molecular quadrupole components are relatively good due to partial cancellation of errors.

TABLE II

Comparison Between Experimental and Calculated Second Moments and Diamagnetic Susceptibilities

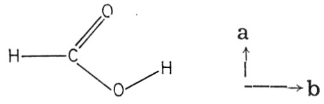
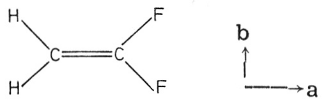
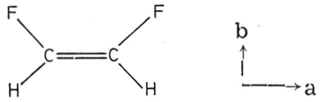
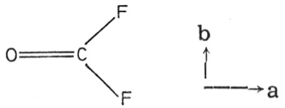
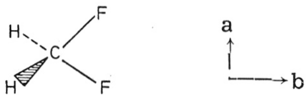
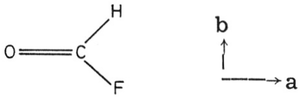
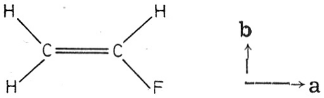
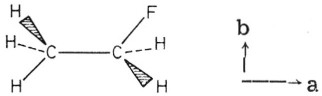
Molecule	Exp. (in 10^{-16} cm²)	SCC	Exp. (in 10^{-6} cm³ mole⁻¹)	SCC
	$\langle a^2\rangle_e = 25.6 \pm 0.3$ $\langle b^2\rangle_e = 7.7 \pm 0.3$ $\langle c^2\rangle_e = 3.5 \pm 0.3$	25.64 7.67 3.09	$\chi^d_{aa} = -47.6 \pm 0.8$ $\chi^d_{bb} = -123.3 \pm 0.8$ $\chi^d_{cc} = -141.4 \pm 0.8$	-45.64 -121.87 -141.29
	$\langle a^2\rangle_e = 31.7 \pm 0.6$ $\langle b^2\rangle_e = 27.1 \pm 0.6$ $\langle c^2\rangle_e = 4.50$	31.66 27.54 4.09	$\chi^d_{aa} = -133.8$ $\chi^d_{bb} = -153.5$ $\chi^d_{cc} = -249.2$	-134.2 -151.7 -251.1
	$\langle a^2\rangle_e = 46.7 \pm 0.7$ $\langle b^2\rangle_e = 18.1 \pm 0.7$ $\langle c^2\rangle_e = 4.50$	47.27 17.83 4.09	$\chi^d_{aa} = -95.6$ $\chi^d_{bb} = -217.3$ $\chi^d_{cc} = -274.9$	-93.0 -217.9 -276.2
	$\langle c^2\rangle_e = 26.1 \pm 0.5$ $\langle c^2\rangle_e = 24.8 \pm 0.5$ $\langle c^2\rangle_e = 4.00$	25.65 24.18 3.31	$\chi^d_{aa} = -122.1$ $\chi^d_{bb} = -127.8$ $\chi^d_{cc} = -216.2$	-116.6 -122.9 -211.4

Table II continued

Molecule	Exp. (in 10^{-16} cm^2)	SCC	Exp. (in 10^{-6} cm^3 mole^{-1})	SCC
	$\langle a^2\rangle_e = 25.8 \pm 0.7$	23.37	$\chi^d_{aa} = -59.2$	-51.3
	$\langle a^2\rangle_e = 9.0 \pm 0.7$	7.68	$\chi^d_{bb} = -130.7$	-117.9
	$\langle c^2\rangle_e = 5.00$	4.41	$\chi^d_{cc} = -147.7$	-131.7
	$\langle a^2\rangle_e = 24.4 \pm 2.0$	24.88	$\chi^d_{aa} = -38.0 \pm 4.7$	-39.6
	$\langle b^2\rangle_e = 6.4 \pm 2.0$	6.58	$\chi^d_{bb} = -114.6 \pm 5.8$	-117.3
	$\langle c^2\rangle_e = 2.6 \pm 2.0$	2.77	$\chi^d_{cc} = -130.6 \pm 5.9$	-133.4
	$\langle a^2\rangle_e = 29.5 \pm 1.6$	30.01	$\chi^d_{aa} = -52.6 \pm 4.2$	-54.3
	$\langle b^2\rangle_e = 8.8 \pm 1.6$	9.25	$\chi^d_{bb} = -140.5 \pm 4.5$	-142.4
	$\langle c^2\rangle_e = 3.6 \pm 1.6$	3.55	$\chi^d_{cc} = -162.5 \pm 4.5$	-166.6
	$\langle c^2\rangle_e = 33.2 \pm 1.9$	33.15	$\chi^d_{aa} = -80.0 \pm 4.7$	-77.4
	$\langle b^2\rangle_e = 11.6 \pm 1.9$	11.36	$\chi^d_{bb} = -171.6 \pm 5.3$	-169.9
	$\langle c^2\rangle_e = 7.2 \pm 1.9$	6.89	$\chi^d_{cc} = -190.3 \pm 5.5$	-188.8

Another property of interest is the magnetic susceptibility χ_{vv}. The total magnetic susceptibility is a sum of diamagnetic and paramagnetic terms

$$\chi_{vv} = \chi^{d}_{vv} + \chi^{p}_{vv} \tag{8}$$

where v = a, b or c. The paramagnetic term χ^{p}_{vv} can be treated either by perturbation methods[15] or by variation-perturbation[16] methods. For the molecules of the size like those considered in this paper this is a rather difficult task and requires a separate study (now in progress).

We shall therefore focus our attention on the diamagnetic term. This term corresponds to the classical Langevin diamagnetism and can be related to second moments in a simple fashion: $\chi^{d}_{aa} = \frac{Ne^2}{4\,mc^2} (< b^2 >_e + < c^2 >_e)$ and cyclic permutations thereof.

Table II exhibits very good agreement with experimental values for χ^{d}_{vv} H_2CF_2 is an exception where the error in χ^{d}_{zz} is about 13%. A good agreement was expected since individual second moments were fairly well reproduced by our SCC wavefunctions. Diamagnetic susceptibilities provide some information about the size of the molecular electronic cloud and SCC method proves to be useful in this respect.

CONCLUSION

The calculated anisotropies in second moments and molecular quadrupoles obtained by the SCC method are in a reasonable agreement with experiment. Comparing present results with those obtained earlier[1,17] we can say that SCC method gives molecular quadrupoles with an accuracy which is comparable with that of the CNDO/2D method* and with *ab initio* minimum basis set calculations. This accuracy is sufficient to allow a correct assignment of the sign of experimental g-values. Second moments of charge and diamagnetic contributions to the total magnetic susceptibility are calculated in very good agreement with experiment. Therefore we draw the conclusion from this work and from earlier work on dipole moments[19] that the SCC method gives reasonably good overall electron distribution in molecules and consequently that eqns. (1) and (2) successfully simulate electronic coulomb repulsions.

Acknowledgement. We thank the UT Computer Center for a generous support in computing time and in technical assistance.

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* In the CNDO/2D method the matrix $\check{C}$ formed by the CNDO/2 eigenvectors is subjected to a $\tilde{S}^{-1/2}\tilde{C}$ transformation where $\tilde{S}$ is a metric matrix.[18]

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IZVOD

Izračunavanje kvadrupolnih momenata nekih fluoriranih ugljikovodika pomoću SCC metode

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Primjenom metode samousaglašene raspodjele elektronskog naboja izračunani su kvadrupolni momenti niza fluoriranih ugljikovodika. Slaganje s eksperimentom je dobro, što ukazuje da primijenjena SCC metoda svojom parametrizacijom uspješno simulira međuelektronsku Coulombsku interakciju.

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Primljeno 27. kolovoza 1972.