Calculation of Molecular Electric Dipole and Quadrupole Moments

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Abstract: A method of calculating molecular electric dipole and quadrupole moments by summing empirically derived atom dipole moments is presented. The electric dipole and quadrupole moments of a large number of molecules are calculated and compared with experiment. The empirical methods are also applied to the evaluation of the second moments of the electronic charge distribution and resultant diagonal elements in the diamagnetic susceptibility tensor.

Electric dipole moments have been useful in understanding charge distributions in molecules. The molecular electric dipole moment is defined by

$$\mu_x = |e|\{\sum_\alpha Z_\alpha x_\alpha - \langle 0|\sum_i x_i|0\rangle\} \tag{1}$$

Z_α is the atomic number of the αth nucleus and z_α and z_i are the coordinates of the nuclei and electrons, respectively. $\langle 0|0\rangle$ indicates the ground electronic state average value. The absolute values of electric dipole moments have been measured in a large number of molecules[1] by a variety of experimental methods,[2-5] and the interpretation of the electric dipole moments has led to information on the reorganizations of the charge distribution when atoms are combined to form molecules.

Molecular dipole moments can be predicted on the basis of the vector sum of *bond* dipole moments.[4]

$$\boldsymbol{\mu} = \sum_\beta \boldsymbol{\mu}_\beta \tag{2}$$

$\boldsymbol{\mu}_\beta$ in eq 2 are the bond dipole moments which are transferrable from one molecule to another. The empirically determined bond moments[4] and their additivities as shown in eq 2 have been very successful in predicting new moments and determining the structures of new molecules.

Recently the molecular Zeeman effect[6] has been developed[7] extensively to measure molecular quadrupole moments, and results are now available for a large number of molecules.[8] Therefore, we have tried to apply empirical additivity concepts to evaluate molecular quadrupole moments. The present paper is an attempt to develop rules to calculate the dipole and quadrupole moments of a molecule.

Owing to the availability of bond dipole moments and the successful combination of bond dipole moments to compute total molecular dipole moments, we will first consider the bond moment approach to compute molecular quadrupole moments. The center of mass (CM) molecular quadrupole moment along the *z* axis is defined by

$$Q_{xx} = \frac{|e|}{2}\{\sum_\alpha Z_\alpha(3x_\alpha{}^2 - r_\alpha{}^2) - \langle 0|\sum_i(3x_i{}^2 - r_i{}^2)|0\rangle\} = \frac{|e|}{2}\{\sum_\alpha Z_\alpha(2x_\alpha{}^2 - y_\alpha{}^2 - z_\alpha{}^2) - \langle 0|\sum_i(2x_i{}^2 - y_i{}^2 - z_i{}^2)|0\rangle\} \tag{3}$$

Now, in order to use a bond moment model we must sum over terms which have their origin at the various bond segments in the molecule. In general, the molecular quadrupole moment at the molecular CM is given in terms of bond dipole and bond quadrupole moments by[9]

$$\mathbf{Q} = \sum_\beta(3\mathbf{R}_\beta\boldsymbol{\mu}_\beta - \mathbf{R}_\beta\cdot\boldsymbol{\mu}_\beta\mathbf{1}) + \sum_\beta \mathbf{Q}_\beta \tag{4}$$

where $\mathbf{R}_\beta$ is the vector from the CM to the origin of the βth bond and $\boldsymbol{\mu}_\beta$ and $\mathbf{Q}_\beta$ are the bond dipole and bond quadrupole moments. There is considerable ambiguity in defining the origin of the bond moment.[10] In order to use eq 4 to predict molecular quadrupole moments, we must assign the values of the bond quadrupole moments and the origins of both the bond dipole and bond quadrupole moments. Bond quadrupole moments are not necessarily small relative to the $R\mu$ term in eq 4. However, if we shift the origin of the moments to the atomic centers and assume (see theory) that the *atom* quadrupole moments are small relative to the corresponding atom $R\mu$ term, the molecular quadrupole moments can then be determined entirely on the basis of *atom* dipoles

$$\mathbf{Q} \cong \sum_a(3\mathbf{R}_a\boldsymbol{\mu}_a - \mathbf{R}_a\cdot\boldsymbol{\mu}_a\mathbf{1}) \tag{5}$$

where the sum over *a* is over all atoms in the molecule. $\mathbf{R}_a$ is vector from the CM to the *a*th atom and $\boldsymbol{\mu}_a$ is the atom dipole moment. Using the same approach we define the total dipole moment as a vector sum of atom dipole moments

$$\boldsymbol{\mu} = \sum_a \boldsymbol{\mu}_a \tag{6}$$

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(1) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(2) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955.

(3) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

(4) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955; "The Determination of Dipole Moments, Physical Methods of Organic Chemistry," Vol. III, A. Weissberger, Ed., Interscience, New York, N. Y., 1960.

(5) R. J. W. Le Fevre, "Dipole Moments," Methuen, London, 1948.

(6) W. Hüttner and W. H. Flygare, *J. Chem. Phys.*, 47, 4137 (1967).

(7) W. Hüttner, M. K. Lo, and W. H. Flygare, *ibid.*, 48, 1206 (1968); W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *ibid.*, 50, 1714 (1969).

(8) W. H. Flygare and R. C. Benson, *Mol. Phys.*, 20, 225 (1971).

(9) A. D. McLean and M. Yoshimine, *J. Chem. Phys.*, 47, 1927 (1967).

(10) A. G. Turner, A. F. Saturno, P. Hauk, and R. G. Parr, *ibid.*, 40, 1919 (1964).

We will use eq 5 and 6 to assign atom dipole moments which can be used in any molecule to evaluate both the total dipole moment and the total quadrupole moment. This approach clearly defines the origin of the individual dipole moments as the atomic origin.

The atom-localized model for molecular dipole and quadrupole moments is also applied to the evaluation of the second moment of the ground-state electronic charge distribution

$$\langle x^2\rangle = \langle 0|\sum_i x_i^2|0\rangle \tag{7}$$

and the corresponding molecular diamagnetic susceptibilities

$$\chi_{xx}{}^{\mathrm{d}} = -\frac{e^2N}{4mc^2}\langle 0|\sum_i(y_i^2 + z_i^2)|0\rangle \tag{8}$$

Theory and Results

The molecular dipole moment, molecular quadrupole moment, second moment of the electronic charge distribution, and the diamagnetic susceptibility are defined in eq 1, 3, 7, and 8, respectively. We will now develop empirical rules for the evaluation of each of these quantities from a localized *atomic* viewpoint. The CM is the reference point.

In any model which attempts to break the molecular moments down into sums over localized contributions, the distribution of electrons in these localized regions must be assigned. The sum over the i electrons in the moment equations can be partitioned in any arbitrary way, without loss in generality. For instance, CH_2F_2 contains 26 electrons. If these electrons are counted in individual sums which contain 1, 1, 9, 9, and 6 electrons, we can write

$$\langle 0|\sum_i \mathbf{r}_i|0\rangle = \sum_n\langle 0|\sum_{i_n=1}^{Z_n}\mathbf{r}_{i_n}|0\rangle_n \tag{9}$$

where nth sum has been associated with the nth nucleus; *e.g.*, in the case of CH_2F_2

$$\langle 0|\sum_i \mathbf{r}_i|0\rangle = 2\langle 0|\sum_{i_\mathrm{H}=1}^{1}\mathbf{r}_{i_\mathrm{H}}|0\rangle_\mathrm{H} + 2\langle 0|\sum_{i_\mathrm{F}=1}^{9}\mathbf{r}_{i_\mathrm{F}}|0\rangle_\mathrm{F} + \langle 0|\sum_{i_\mathrm{C}=1}^{6}\mathbf{r}_{i_\mathrm{C}}|0\rangle_\mathrm{C} \tag{10}$$

In each of these individual sums we can then use the transformation illustrated in Figure 1.

$$\mathbf{r}_{i_n} = \mathbf{r}_n + \boldsymbol{\rho}_{i_n} \tag{11}$$

to give

$$\langle 0|\sum_i \mathbf{r}_i|0\rangle = \sum_n\langle 0|\sum_{i_n}^{Z_n}(\mathbf{r}_n + \boldsymbol{\rho}_{i_n})|0\rangle_n = \sum_n\langle 0|\sum_{i_n}^{Z_n}\mathbf{r}_n|0\rangle_n + \sum_n\langle 0|\sum_{i_n}^{Z_n}\boldsymbol{\rho}_{i_n}|0\rangle_n \tag{12}$$

The integral of a sum equals the sum of integrals which gives

$$\langle 0|\sum_i \mathbf{r}_i|0\rangle = \sum_n\sum_{i_n}^{Z_n}\langle 0|\mathbf{r}_n|0\rangle_n + \sum_n\sum_{i_n}^{Z_n}\langle 0|\boldsymbol{\rho}_{i_n}|0\rangle_n \tag{13}$$

Applying the Born-Oppenheimer approximation to the nuclear term in eq 13 and assuming the molecule is a rigid rotor gives

$$\sum_{i_n}^{Z_n}\langle 0|\mathbf{r}_n|0\rangle_n = Z_n\mathbf{r}_n$$

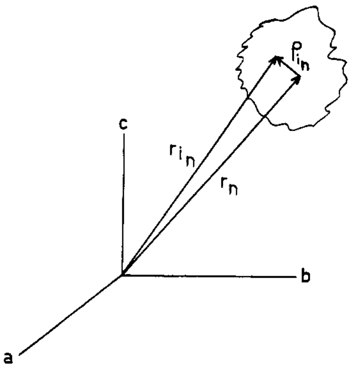

Figure 1. The coordinate system showing the vectors from the molecular center of mass to the nth atomic nucleus, $\mathbf{r}_n$, and the ith electron in the nth atom. ρ_{i_n} is the vector from the nth atom nucleus to the ith electron in the atom.

and defining

$$\sum_{i_n}^{Z_n}\langle 0|\boldsymbol{\rho}_{i_n}|0\rangle_n$$

as $\langle\boldsymbol{\rho}\rangle_n$ gives

$$\langle 0|\sum_i \mathbf{r}_i|0\rangle = \sum_n Z_n\mathbf{r}_n + \sum_n\langle\boldsymbol{\rho}\rangle_n \tag{14}$$

The above discussion is quite general, as all electrons are included in the sum of $\langle 0|\boldsymbol{\rho}_{i_n}|0\rangle$ matrix elements. The $\boldsymbol{\rho}_{i_n}$ operator which originates at the nth nucleus can extend throughout the molecule. However, we will now assume that the $\boldsymbol{\rho}_{i_n}$ operator is localized at the nth atom. This assumption indicates that atoms in molecules maintain a major share of their free-atom electron densities. This viewpoint is substantiated by free atom-molecule difference density plots which indicate a relatively small electron reorganization when free atoms form molecules.[11] If the electrons in a bonded atom are assumed to be localized, $\langle\boldsymbol{\rho}\rangle_n$ represents the dipole polarization of the electronic charge on nucleus n, or the *atom dipole*.

The square of electronic coordinates can be treated in the same way.

$$\begin{aligned}\langle 0|\sum_i r_i^2|0\rangle &= \sum_n\langle 0|\sum_{i_n=1}^{Z_n}r_{i_n}{}^2|0\rangle_n = \sum_n\langle 0|\sum_{i_n}^{Z_n}(\mathbf{r}_n + \boldsymbol{\rho}_{i_n})^2|0\rangle_n = \\ &\sum_n\langle 0|\sum_{i_n}^{Z_n}(r_n{}^2 + 2\mathbf{r}_n\cdot\boldsymbol{\rho}_{i_n} + \rho_{i_n}{}^2)|0\rangle_n = \\ &\sum_n\langle 0|\sum_{i_n}^{Z_n}r_n{}^2|0\rangle_n + \sum_n\langle 0|\sum_{i_n}^{Z_n}2\mathbf{r}_n\cdot\boldsymbol{\rho}_{i_n}|0\rangle_n + \sum_n\langle 0|\sum_{i_n}^{Z_n}\rho_{i_n}{}^2|0\rangle_n\end{aligned} \tag{15}$$

Rearranging as before gives

$$\begin{aligned}\langle 0|\sum_i r_i^2|0\rangle &= \sum_n\sum_{i_n}^{Z_n}\langle 0|r_n{}^2|0\rangle_n + \sum_n\sum_{i_n}^{Z_n}\langle 0|2\mathbf{r}_n\cdot\boldsymbol{\rho}_{i_n}|0\rangle_n + \sum_n\sum_{i_n}^{Z_n}\langle 0|\rho_{i_n}{}^2|0\rangle_n = \\ &\sum_n Z_nr_n{}^2 + \sum_n 2\mathbf{r}_n\cdot\sum_{i_n}^{Z_n}\langle 0|\boldsymbol{\rho}_{i_n}|0\rangle_n + \sum_n\sum_{i_n}^{Z_n}\langle 0|\rho_{i_n}{}^2|0\rangle_n\end{aligned} \tag{16}$$

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(11) See, for instance, R. F. W. Bader, I. Keavery, and P. E. Cade, *J. Chem. Phys.*, 47, 3381 (1968).

Defining

$$\sum_{i_n}^{Z_n}\langle 0|\rho_{i_n}{}^2|0\rangle_n$$

as $\langle\rho^2\rangle_n$ and using the definition of atom dipoles in eq 14 gives

$$\langle 0|\sum_i r_i{}^2|0\rangle = \sum_n Z_n r_n{}^2 + \sum_n 2\mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n + \sum_n\langle\rho^2\rangle_n \quad (17)$$

Again if the electrons in bonded atoms are localized, $\langle\rho^2\rangle_n$ represents the average squared electronic distance from the *n*th nucleus and should be proportional to the average diamagnetic susceptibility of that atom.

It is easy to show that both eq 14 and 17 are also satisfied by the Cartesian components of each vector

$$\langle 0|\sum_i x_i|0\rangle = \sum_n Z_n x_n + \sum_n\langle x\rangle_n \quad (18)$$

and

$$\langle 0|\sum_i x_i{}^2|0\rangle = \sum_n Z_n x_n{}^2 + \sum_n 2x_n\langle x\rangle_n + \sum_n\langle x^2\rangle_n \quad (19)$$

where $\langle x\rangle_n$ and $\langle x^2\rangle_n$ are the Cartesian components of $\langle\boldsymbol{\varrho}\rangle_n$ and $\langle\rho^2\rangle_n$ along the x axis. Substituting the results of eq 14, 17, 18, and 19 into eq 1, 3, 7, and 8 gives

$$\mu_x = -|e|\sum_n\langle x\rangle_n \quad (20)$$

$$Q_{xx} = -\frac{|e|}{2}\{\sum_n 2(3x_n\langle x\rangle_n - \mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n) + \sum_n(3\langle x^2\rangle_n - \langle\rho^2\rangle_n)\} \quad (21)$$

$$\langle 0|\sum_i x_i{}^2|0\rangle = \sum_n Z_n x_n{}^2 + \sum_n 2x_n\langle x\rangle_n + \sum_n\langle x^2\rangle_n \quad (22)$$

$$\chi_{xx}{}^d = -\frac{e^2N}{4mc^2}\{\sum_n Z_n(y_n{}^2 + z_n{}^2) + 2\sum_n(y_n\langle y\rangle_n + z_n\langle z\rangle_n) + \sum_n(\langle y^2\rangle_n + \langle z^2\rangle_n)\} \quad (23)$$

$3\langle x^2\rangle_n - \langle\rho^2\rangle_n$ is the atom quadrupole moment, by analogy with $\langle x\rangle_n$ (the atom dipole moment). If the molecular structure of a molecule is known, the quantities in eq 20–23 may be calculated if values of $\langle x\rangle_n$ and $\langle x^2\rangle_n$ for each atom can be found. Equations 20 and 21 are identical with eq 6 and 4, respectively.

Note that for planar molecules the out-of-plane electronic second moment is defined by eq 22 to be

$$\langle 0|\sum_i c_i{}^2|0\rangle = \sum_n\langle c^2\rangle_n \quad (24)$$

where the c_i's are the out-of-plane electronic coordinates. Blickensderfer, Wang, and Flygare[12] have previously deduced empirical rules for evaluating $\langle c^2\rangle$ for a planar molecule which give excellent agreement with the experimental results. Malli and Fraga[13] have calculated the diamagnetic susceptibilities of many free atoms, from which values of $\langle 0|r^2/3|0\rangle_n$ can be obtained. If the electronic charge distribution in bonded atoms is not too different from the free-atom distribution, then the empirical values of $\langle c^2\rangle_n$ obtained by Blickensderfer, *et al.*, should be approximately equal to the $\langle 0|\Sigma_i r_i{}^2/3|0\rangle_n$ values of Malli and Fraga. A comparison is made in Table I. The agreement should not really be surprising, since close inspection of electron density maps[11] in bonded atoms reveals that changes in density with respect to the free-atom distribution are relatively large only when the absolute electron density is relatively small. In other words, it appears that the charge distribution in atoms is not dramatically changed by covalent bonding.

Table I. Average Values of Out-of-Plane $\langle c^2\rangle$ in Molecules Compared to the Corresponding Free-Atom Values

Atom	Rules[a] for $\langle c^2\rangle_n$	Calculation[b] of $\langle r^2/3\rangle_n$
H	0.25	0.28
C	1.0	1.28
N	1.0	1.12
O	1.0	1.04
F	1.0	0.95

[a] Reference 12. [b] Reference 13.

Thus we might expect that the electric quadrupole moment of a bonded atom would be similar to the quadrupole moment of the free atom. Unfortunately, only a few free-atom quadrupole moments are available.[14] Guberman, *et al.*,[14a] have calculated the quadrupole moment of oxygen in the ^{3}P state to be -1.27×10^{-26} esu cm^2. This moment arises from the asymmetric charge distribution in the p orbitals, where two p orbitals are singly occupied and the third is doubly occupied. When oxygen is in a bonding situation, the singly occupied orbitals will be more completely filled and will result in a more symmetric charge distribution. In the limit of ionic bonding, the electronic configuration will be like neon which by symmetry has a zero atom quadrupole moment. Furthermore, both the sp^3 carbon atom and 1s hydrogen are highly symmetric and will have near zero quadrupole moments.

With these thoughts in mind, we will assume that the atom quadrupole moments in eq 21 are small relative to the atom dipole term which is weighted by the distance from the CM to the atom. This assumption will be less valid for heavier atoms, since the larger orbitals will produce larger effects when asymmetrically occupied. This assumption is however supported by the relative magnitudes of the dipole and quadrupole polarizabilities of atoms and ions.[15] For example, molecular electric fields and field gradients of 10^6 esu/cm^2 and 10^{14} esu/cm^3, respectively, will produce an induced-atom dipole in fluorine[15b] of ~0.1 e Å and an induced-atom quadrupole[15c] of $\sim 0.7 \times 10^{-26}$ esu cm^2. The above atom dipole is comparable to those in Table II.

We will therefore write eq 21 as

$$Q_{xx} \cong -\frac{|e|}{2}\sum_n 2(3x_n\langle x\rangle_n - \mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n) \quad (25)$$

which is identical with eq 5. We can now use eq 20 (or see eq 6) and eq 25 (or see eq 5) and experimental values of molecular dipole moments and molecular quadrupole moments to assign the atom dipoles. The atom dipoles can then be used to predict the dipole

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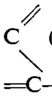
(12) R. P. Blickensderfer, J. H. S. Wang, and W. H. Flygare, *J. Chem. Phys.*, **51**, 3196 (1969).

(13) G. Malli and S. Fraga, *Theor. Chim. Acta*, **5**, 284 (1966).

(14) (a) S. L. Guberman and W. A. Goddard III, *J. Chem. Phys.*, **53**, 1803 (1970); (b) J. R. P. Angel, P. G. H. Sanders, and G. K. Woodgate, *ibid.*, **47**, 1552 (1967); (c) T. A. Miller and R. S. Freund, *Phys. Rev. A*, **4**, 81 (1971).

(15) (a) G. Burns, *J. Chem. Phys.*, **31**, 1253 (1959); *Phys. Rev.*, **115**, 357 (1959); (b) J. Thorhallsson, C. Fisk, and S. Fraga, *Theor. Chim. Acta*, **10**, 388 (1968); (c) P. W. Langhoff and R. P. Hurst, *Phys. Rev. A*, **739**, 1415 (1965), quadrupole polarizability obtained by extrapolation.

Table II. The Reduced-Atom Dipoles, $\langle x \rangle_n$ (Å)^a

	Hydrogen	
1.	H—C<	+0.20
2.	H—C═C	+0.15
3.	H—C≡C	+0.06
4.	H—C≡N	+0.06
5.	H—C═O	+0.05
6.	H—O	+0.30
7.	H—X (halogen)	+0.31
8.	H—N	+0.25
9.	H—C (aromatic)	+0.16
	Fluorine	
1.	F—C<	−0.15
2.	F—C═C	−0.13
3.	F—C≡C, F—C≡N	−0.10
4.	F—H	−0.07
5.	F—C (aromatic)	−0.13
6.	F—C═O	(−0.20 to −0.29)
	sp^3 Carbon	
1.	C—H	0
2.	C—F	0.0 to +0.03
3.	C—C═C	0
4.	C—C═O	0
5.	C—O	0.06 to 0.08
6.	C—C	0
	sp^2 Carbon	
1.	C═C	+0.02 to +0.05
2.	═C—H, ═C—C, ═C-	0
3.	C═O	+0.15
4.	 (aromatic)	−0.16
5.	═C—F	+0.02
6.	═C—O	≈0
	sp Carbon	
1.	C≡C	+0.30
2.	C≡N	+0.39
3.	O═C*═O	0.0
4.	X═C*═O	−0.02 to −0.07
	sp^2 Oxygen	
1.	O═C<	−0.28
2.	O═C═X	−0.10
3.	O═C═O	−0.20
	sp^3 Oxygen	
1.	O—H	−0.02
2.	O—C (sp^3) (C_2 axis)	−0.10
3.	O—C (sp^2) (C_2 axis)	−0.12
4.	O—C (sp)	−0.15
	Nitrogen	
1.	N≡C	−0.17
2.	NH$_3$	+0.03 (C_3 axis)
	Chlorine	
1.	Cl—C≡	−0.02

[a] Used with eq 6 or 20 to calculate the molecular dipole moments and with eq 5 or 25 to compute the molecular quadrupole moments. The plus sign means that the electrons in the nth atom are polarized away from that atom into the bond.

moments (and signs) and quadrupole moments of new molecules. We use the following conventions in assigning the atom dipole moments. (1) Bonded atoms are always polarized collinear with the bond. (2) Atoms bonded to just one other atom will be chosen to be polarized into the bond if the atom dipole is positive. (3) Atoms bonded to more than one other atom will be chosen to be polarized into the bond of highest order, *e.g.*, an sp^2 carbon will be polarized into the double bond. (4) sp^3 carbon atoms will be chosen to be polarized toward the most electronegative substituent. The exact direction is determined by symmetry. The first convention is quite reasonable, since by symmetry the average electronic coordinate perpendicular to a bond must be zero. The other conventions are also dictated by symmetry considerations and reduce the number of variables which must be considered.

The atom dipoles given in Table II were deduced from the molecules in Table III marked with a dagger. For example, in the case of water there are three independent experimental moments which can be expressed in terms of atom dipoles by eq 20 and 25. However, there are only two atom dipoles and these were found by simultaneously solving the above equations. The variation in the sp^3 and sp^2 carbon atoms arises from the difficulty in assigning a single-atom dipole to atoms which are multiply bonded. Molecular moments calculated from these atom dipoles are compared with known values in Table III. The calculated dipole moment signs are also given. In some cases carbon atom dipoles were chosen to fit the molecular dipole. This normally implied a change in calculated dipole of 0.3 D. The same effect could be obtained by hybridization effects (see Discussion).

The atom dipoles can also be used with values for $\langle 0|r^2/3|0\rangle_n$ obtained from the free-atom diamagnetic calculations of Malli and Fraga,[13] as shown in Table IV, and the known molecular structures, to evaluate the second moments of electronic charge and diamagnetic susceptibilities using eq 22 and 23. The results are given in Table V along with the known experimental results.

Discussion

The resultant calculated molecular dipole and quadrupole moments given in Table III are in reasonable agreement with the experimental values. However, it should be pointed out that there is some difficulty in choosing the proper atom dipoles associated with sp^2 and sp^3 carbons. This is illustrated in Table VI by two examples, trimethylene oxide and methylene fluoride. The first two columns give the calculated moments when normal sp^3 carbon hybridization was assumed. The deviation of the moments from experimental moments is as large as 50%. The calculation can be improved by using the measured $J_{^{13}\mathrm{CH}}$ coupling constants. For trimethylene oxide[16] J_α is 148 and J_β is 137.3 Hz, and for methylene fluoride[17] J is 185 Hz. It has been shown[17] that these coupling constants can be related to the amount of s character in the carbon–hydrogen bond. The estimated hybridization indicates that the α carbon in trimethylene oxide and the carbon in methylene fluoride are more nearly sp^2 in character than the previously assumed sp^3. With this difference, a new set of estimated moments was calculated and the agreement with experiment was considerably improved (see Table VI).

If the hybridization is known, we believe the atom dipoles given in Table II will be accurate to within 0.02 Å. The corresponding uncertainties in the molecular electric moments calculated with eq 20 and 21 will depend on the structure of the particular molecule. As an

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(16) P. Laszlo, *Bull. Soc. Chim. Fr.*, 558 (1966), and references cited therein.

(17) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 37, 2198 (1962), and references cited therein.

Table III. Calculated Molecular Dipole Moments (Eq 6 or 20) and Calculated Molecular Quadrupole Moments (Eq 5 or 25) Compared with Experimental Results^{a}

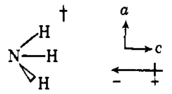
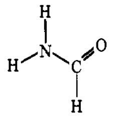
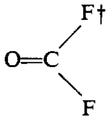
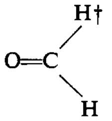
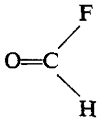
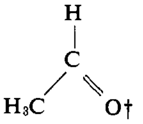
Molecule $\overset{b}{\uparrow}\!\lfloor\!\rightarrow a$	μ_a μ_b μ_c Exptl	Calcd	Q_{aa} Q_{bb} Q_{cc} Exptl	Calcd
	0	0	+1.2 ± 0.1	+1.3
	0	0	+1.2 ± 0.1	+1.3
	|1.47|	+1.44	−2.4 ± 0.1	−2.6
	|3.62|	−2.96	−0.3 ± 0.5	−0.5
	|0.85|	−0.73	+3.4 ± 0.4	+3.2
	0	−0.33	−3.1 ± 0.8	−2.7
H—C≡N	|2.98|	−2.98	+2.6^{b}	+2.0
	0	0	−1.3	−1.0
	0	0	−1.3	−1.0
CH_3—C≡N† $\overset{+\;\;-}{\longmapsto}$	−3.91	−3.65	−1.8 ± 1.2	−1.0
	0		+0.9 ± 1.2	+0.5
	0		+0.9 ± 1.2	+0.5
Cl—C≡N	−2.80	−2.78	−4.0 ± 0.9^{c}	−5.0
	0	0	+2.0 ± 0.9	+2.5
	0	0	+2.0 ± 0.9	+2.5
Br—C≡N	|2.94|	−3.02^{d}	−6.0 ± 1.1^{e}	−7.8
	0	0	+3.0 ± 1.1	+3.9
	0	0	+3.0 ± 1.1	+3.9
F—C≡N	|2.17|	−2.20	−4.2^{b}	−3.8
	0	0	+2.1	+1.9
	0	0	+2.1	+1.9
I—C≡N	|3.71|	−3.46^{d}	−7.4 ± 1.1^{c}	−9.6
	0	0	+3.7 ± 1.1	+4.8
	0	0	+3.7 ± 1.1	+4.8
N≡C—C≡N	0	0	−9.0^{b}	−11.2
	0	0	4.5	+5.6
	0	0	4.5	+5.6
	|0.95|	+0.64	−3.7 ± 0.7	−3.1
	0	0	−0.2 ± 0.5	−0.8
	0	0	+3.9 ± 1.1	+3.9
	+2.34	+2.30	−0.1 ± 0.3	−0.2
	0	0	+0.2 ± 0.2	+0.7
	0	0	−0.1 ± 0.5	−0.5
O═C═S	+0.71	+0.72^{d}	−0.8 ± 0.2	−1.0
	0	0	+0.4 ± 0.2	+0.5
	0	0	+0.4 ± 0.2	+0.5
	|0.60|	+0.71	−4.5 ± 0.2	−4.5
	|1.93|	−1.82	+2.6 ± 0.2	+2.6
	0	0	+1.9 ± 0.4	+1.9
O═C═O†	0	0	−4.4 ± 0.2	−4.4
	0	0	+2.2 ± 0.2	+2.2
	0	0	+2.2 ± 0.2	+2.2
O═C═Se	+0.75	+0.77^{d}	−0.4 ± 0.2	−0.4
	0	0	+0.2 ± 0.2	+0.2
	0	0	+0.2 ± 0.2	+0.2
	|2.98|	−3.23	−9.4 ± 1.2	−8.8
	0	0	+4.5 ± 1.1	3.6
	0	0	+4.9 ± 1.7	5.2
	|2.55|	−2.54	−1.2 ± 1.5	−2.9
	|0.87|	+0.93	+1.0 ± 0.9	+1.9
	0	0	+0.2 ± 1.8	+1.0
H—C≡C—H	0	0	+7.2^{b}	5.4
	0	0	−3.6	−2.7
	0	0	−3.6	−2.7
H—C≡C—F†	|0.75|	−0.77	+4.0 ± 0.2	+3.8
	0	0	−2.0 ± 0.2	−1.9
	0	0	−2.0 ± 0.2	−1.9

Table III (*Continued*)

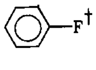
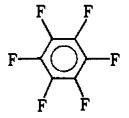
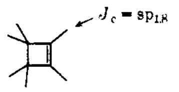
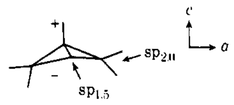
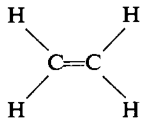
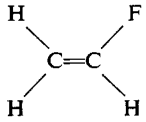
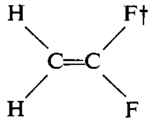
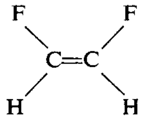
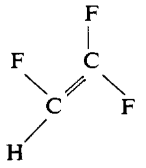
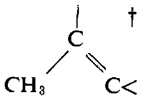
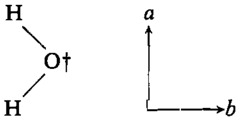
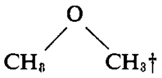
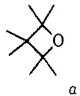
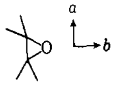
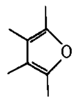
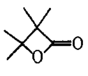
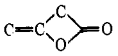
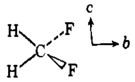
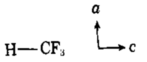
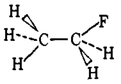
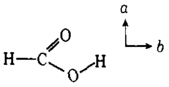
Molecule b ↑ → a	μ_a μ_b μ_c Exptl	Calcd	Q_{aa} Q_{bb} Q_{cc} Exptl	Calcd
CH_3—C≡C—H†	−0.75 0 0	−0.69 0 0	+4.8 ± 0.2 −2.4 ± 0.2 −2.4 ± 0.2	+5.0 −2.5 −2.5
CH_3—C≡C—C≡C—H	. . . 0 0	−0.69 0 0	+9.8 ± 0.8 −4.9 ± 0.8 −4.9 ± 0.8	+12.2 −6.6 −6.6
	0 0 0	0 0 0	+2.8 ± 1.4 +2.8 ± 1.4 −5.6 ± 2.8	+3.3 +3.3 −6.6
	$\lvert 1.66\rvert$ 0 0	−1.34 0 0	−1.9 ± 0.8 +5.1 ± 1.0 −3.2 ± 1.0	−2.1 +6.1 −4.0
	0 $\lvert 0.42\rvert$ 0	0 −0.44 0	+1.4 ± 0.4 +3.7 ± 0.4 −5.1 ± 0.5	+2.2 +4.7 −6.9
	0 0 0	0 0 0		−8.6 −8.6 +17.2
	$\lvert 0.13\rvert$ 0 0	−0.64 0 0	−0.3 ± 0.6 +1.6 ± 0.7 −1.3 ± 1.0	−0.6 2.4 −1.8
	0 0 $\lvert 0.67\rvert$	0 0 +0.67^e	+1.3 ± 0.6 −2.6 ± 0.3 +1.3 ± 0.4	+2.0 −4.0 +2.0
	+0.45 0 0	+0.46^e 0 0	−0.4 ± 0.4 +2.4 ± 0.3 −2.0 ± 0.6	−0.3 +2.4 −2.1
H—C≡C—Cl†	$\lvert 0.44\rvert$ 0 0	−0.38 0 0	+7.8^b −3.9 −3.9	+4.6 −2.3 −2.3
	0 0 0	0 0 0	+2.0 ± 0.2^f	+1.8 +2.5 −4.3
	$\lvert 1.28\rvert$ $\lvert 0.63\rvert$ 0	−1.15 −0.65 0	−0.2 ± 0.2 +3.1 ± 0.2 −2.9 ± 0.3	−0.3 +3.3 −3.0
	$\lvert 1.39\rvert$ 0 0	−1.44 0 0	+2.4 ± 0.5 −0.9 ± 0.4 −1.5 ± 0.8	+2.2 −0.6 −1.6
	0 $\lvert 2.42\rvert$ 0	0 −2.40 0	−1.7 ± 0.4 +3.0 ± 0.3 −1.3 ± 0.5	−0.6 +2.3 −1.7
	$\lvert 0.10\rvert$ $\lvert 1.40\rvert$ 0	−0.11 −1.36 0	−3.5 ± 0.3 +2.7 ± 0.4 +0.8 ± 0.5	−3.3 +2.3 +1.0
	$\lvert 0.36\rvert$ $\lvert 0.05\rvert$ 0	−0.34 −0.05 0	+0.6 ± 0.3 +2.9 ± 0.5 −3.5 ± 0.7	+2.1 +2.2 −4.3

Table III (*Continued*)

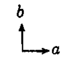
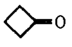
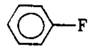
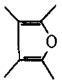
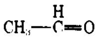
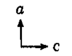
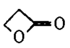
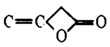
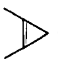
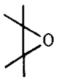
Molecule	μ_a, μ_b, μ_c Exptl	μ_a, μ_b, μ_c Calcd	Q_{aa}, Q_{bb}, Q_{cc} Exptl	Q_{aa}, Q_{bb}, Q_{cc} Calcd
	0 −1.84 0	0 −1.87 0	+2.6 ± 0.1 −0.1 ± 0.1 −2.5 ± 0.1	+2.5 +0.0 −2.5
	0 |1.30| 0	0 −2.06 0	+3.3 ± 0.6 −2.0 ± 0.5 −1.3 ± 1.0	3.00 −2.1 −0.9
H—C≡C—C≡N	|3.60| 0 0	−2.98 0 0		−0.26 +0.13 +0.13
	|1.93| 0 0	−2.16 0 0	−4.8 ± 0.5 +2.3 ± 0.7 +2.5 ± 1.0	−4.8 +2.3 +2.5
	0 |1.88| 0	0 −1.85[e] 0	+2.5 ± 0.4 −4.3 ± 0.5 +1.8 ± 0.8	+2.3 −5.5 +2.2
	|0.66| 0 0	−1.05 0 0	+0.2 ± 0.4 +5.9 ± 0.3 −6.1 ± 0.4	+1.2 +5.6 −6.8
	|3.67| |1.99| 0	−3.17 +1.84 0	−3.1 ± 0.3 −1.9 ± 0.4 +5.0 ± 0.6	−4.8 −0.3 +5.1
	|3.03| |2.24| 0	−3.05 +1.98 0	−2.5 ± 0.3 +1.5 ± 0.4 +1.0 ± 0.6	−5.7 +3.9 +1.8
H—F†	−1.82 0 0	−1.82 0 0	+2.6[b] −1.3 −1.3	+2.6 −1.3 −1.3
CH_3—F†	|1.82| 0 0	−1.60 0 0	−1.4 ± 1.1 +0.7 ± 0.6 +0.7 ± 0.6	−1.6 +0.8 +0.8
	0 |1.96| 0	0 −1.92 0	−4.1 ± 0.3 +1.9 ± 0.4 +2.2 ± 0.6	−4.8 +1.9 +2.9
	0 0 −1.64	0 0 −1.68	−1.8 ± 1.0 −1.8 ± 1.0 +3.6 ± 2.0	−2.5 −2.5 +5.0
CH_3—CH_3	0 0 0	0 0 0	−0.8 ± 0.1[f] +0.4 ± 0.1 +0.4 ± 0.1	−1.2 +0.6 +0.6
	|1.69| |1.00| 0	−1.32 −0.94 0	−2.0 ± 0.4 +1.3 ± 0.4 +0.7 ± 0.7	−3.0 +0.8 +2.2
	|1.39| |0.26| 0	−1.02 0 0	−5.3 ± 0.4 +5.2 ± 0.4 +0.1 ± 0.4	−6.0 +5.8 −0.2

[a] The experimental dipole moments are from ref 1 and the experimental quadrupole moments are from ref 8. The molecules marked with a dagger were used to obtain the atom dipoles in Table II. The units of μ and Q are 10^{-18} esu cm and 10^{-26} esu cm^2, respectively. [b] M. Krause, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, No. 438 (1967), and references cited therein. [c] H. L. Tigelaar, J. J. Ewing, and W. H. Flygare, unpublished. [d] Heavy atom used to fit dipole. [e] Carbon chosen to fit dipole (see text) [f] A. D. Buckingham, R. L. Disch, and D. A. Dunmur, *J. Amer. Chem. Soc.*, **90**, 3104 (1968).

Table IV. Average Free-Atom Values (10^{-16} cm^2) of $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$ from Ref 13

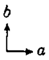
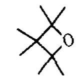
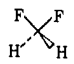
H	0.25	O	1.0	P	2.8	Se	3.8
C	1.2	F	1.0	S	2.7	Br	3.6
N	1.1	Si	3.0	Cl	2.6		

Table V. Average Values of $\langle a^2 \rangle$, $\langle b^2 \rangle$, and $\langle c^2 \rangle$ (10^{-16} cm^2) in Several Molecules[a] and Values of the Diamagnetic Susceptibility Tensor Elements [10^{-6} erg/(G^2 mol)][b]

Molecule 	$\Sigma_n Z_n a_n^2$ $\Sigma_n Z_n b_n^2$ $\Sigma_n Z_n c_n^2$	$\langle a^2 \rangle$ $\langle b^2 \rangle$ $\langle c^2 \rangle$ Exptl	Calcd	χ_{aa}^d χ_{bb}^d χ_{cc}^d Exptl	Calcd
$CH_3—CH═CH_2$	33.52 7.58 1.54	37.5 ± 0.5 11.2 ± 0.5 6.1 ± 0.5	37.1 11.2 6.1	−73.3 ± 1.3 −184.8 ± 1.6 −206.6 ± 1.7	−73.3 −183.5 −205.3
	36.4 36.3 1.6	42.3 ± 2.2 41.8 ± 2.2 8.4 ± 2.2	42.3 41.9 8.5	−213.0 ± 5.8 −214.8 ± 5.0 −356.9 ± 5.1	−214.0 −216.0 −358.0
$H—C≡C—F$	28.34 0 0	31.5 ± 0.6 3.5 ± 0.6 3.5 ± 0.6	31.0 3.5 3.5	31.0 147.9 147.9	−31.0 −147.9 −147.9
	55.3 26.9 4.9	63.2 ± 1.8 32.8 ± 1.8 10.8 ± 1.8	62.4 32.6 10.4	−185.0 ± 3.9 −314.1 ± 5.2 −407.5 ± 5.6	−182.4 −309.1 −403.4
$CHF═CF_2$	62.40 24.00 0	68.2 ± 4.8 29.2 ± 4.8 5.3 ± 4.8	68.6 29.4 5.6	−145.7 ± 10.6 −312.1 ± 10.7 −413.1 ± 10.8	−149.0 −315.0 −417.0
H_2O	1.14 0.57 0	1.9 ± 0.7 1.7 ± 0.7 1.4 ± 0.7	1.9 1.7 1.5	−13.4 ± 1.0 −14.3 ± 1.0 −15.4 ± 1.0	−13.4 −14.6 −15.3
OCO	21.64 0 0	25.5 ± 1.0 2.9 ± 1.0 2.9 ± 1.0	25.5 3.2 3.2	−24.9 ± 3.0 −120.6 ± 2.0 −128.6 ± 2.0	−27.6 −122.0 −122.0
OCS	41.5 0 0	46.2 ± 0.6 4.5 ± 0.6 4.5 ± 0.6	46.7 5.0 5.0	−38.6 ± 2.0 −215.5 ± 2.0 −215.5 ± 2.0	−41.6 −218.0 −218.0
CH_3F	10.54 1.66 1.66	13.0 ± 0.7 3.9 ± 0.7 3.9 ± 0.7	13.3 4.0 4.0	−33.1 ± 1.6 −71.9 ± 1.8 −71.9 ± 2.3	−34.1 −73.0 −73.5
	53.6 53.6 0	60.1 ± 1.5 60.1 ± 1.5 7.7 ± 1.2	60.8 60.8 8.7	−286.0 ± 10.0 −286.0 ± 10.0 −508.0 ± 20.0	−295.0 −295.0 −516.0
	103.6 53.6 0	111.8 ± 0.7 60.8 ± 0.7 8.4 ± 0.7	112.9 61.8 9.4	−293.3 ± 1.7 −509.7 ± 3.6 −732.4 ± 5.0	−302.3 −519.0 −741.0
	30.2 32.6 0.0	36.2 ± 0.7 37.8 ± 0.7 6.8 ± 0.7	36.0 37.7 6.8	−189.5 ± 1.8 −182.5 ± 1.8 −313.9 ± 1.8	−188.0 −182.0 −314.0
 $CH_3—\overset{H}{C}═O$	28.9 5.5 1.5	32.3 ± 0.5 9.6 ± 0.4 5.6 ± 0.5	32.5 9.3 5.4	−64.1 ± 1.4 −160.4 ± 1.8 −177.4 ± 1.8	−62.5 −160.1 −177.0
CH_3CN	30.77 1.64 1.64	34.7 ± 0.4 5.2 ± 0.3 5.2 ± 0.3	34.6 5.3 5.3	−44.2 ± 0.5 −169.4 ± 1.1 −169.4 ± 1.1	−44.5 −169.3 −169.3
NH_3 	1.34 1.34 0.31	2.6 ± 0.4 2.6 ± 0.4 1.9 ± 0.4	2.5 2.5 2.0	−19.3 ± 1.4 −19.3 ± 1.4 −22.0 ± 1.4	−19.2 −19.2 −21.5
	50.77 22.51 3.24	57.2 ± 4.0 28.8 ± 4.0 8.6 ± 4.0	57.6 28.7 8.6	−158.9 ± 6.0 −279.6 ± 6.0 −365.5 ± 6.0	−158.6 −280.9 −366.3
	100.0 25.0 1.6	107.6 ± 6.0 32.1 ± 6.0 8.7 ± 6.0	108.8 32.0 8.8	−173.0 ± 9.0 −493.7 ± 18.7 −592.7 ± 19.0	−172.9 −497.0 −595.0
 calc	13.91 10.03 1.67	17.8 ± 0.2 13.5 ± 0.2 5.8 ± 0.2	17.8 13.5 5.8	−82.3 ± 0.4 −100.4 ± 0.4 −133.4 ± 0.4	−82.2 −100.5 −133.0
	12.89 9.07 3.38	16.3 ± 0.4 13.3 ± 0.4 6.8 ± 0.4	16.4 13.5 6.8	−85.4 ± 0.9 −97.7 ± 1.1 −125.4 ± 2.0	−85.5 −98.2 −126.0

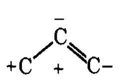
[a] From eq 22 and the atom dipoles in Table II. The experimental results are obtained from ref 8. [b] Molecular structures are obtained from the original Zeeman work referenced in ref 8.

Table VI. Calculated Molecular Dipole and Quadrupole Moments in Trimethylene Oxide and Methylene Fluoride for Two Choices of the Carbon Atom Hybridization

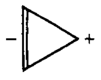
	μ sp³ hybridization	Q	μ Hybridization detd by $J_{^{13}\mathrm{CH}}$	Q	μ Exptl	Q
	−1.95	−6.8	−2.16	−4.4	|1.93|	−4.8
	0	+4.2	0	+2.1	0	+2.3
	0	+2.6	0	+2.3	0	+2.5
	0	−4.8	0	−4.2	0	−4.1
	−1.92	+1.9	−1.82	+2.0	|1.92|	+1.9
	0	+2.9	0	+2.2	0	+2.2

example we estimate the uncertainties in trifluoroethene to be $\mu_a = \pm 0.1$ D, $\mu_b = \pm 0.3$ D, and $Q = \pm 0.7 \times 10^{-26}$ esu cm².

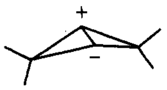
The signs of the dipole moments in several interesting molecules are shown in I–IV. The signs of the dipole of cyclopropene has been measured by Benson and Flygare[18] and the sign in bicyclobutane was calculated by Schulman and Fizanick with an extended Gaussian basis.[19] In both cases, the sign determined by the atom dipole moments agrees with the results in the literature. The dipole moment sign in propene is in disagreement with the sign obtained by a simple vector model[20] (group approach). Again it should be emphasized that small deviations in hybridization as in small strained rings may limit the accuracy of the atom dipole model.



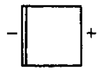
I



II



III



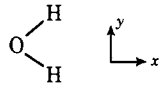
IV

$$\Omega_{xxx} = -|e| \sum_n \Big\{ \langle x\rangle_n \Big(3x_n{}^2 - \frac{3}{2}y_n{}^2 - \frac{3}{2}z_n{}^2\Big) - 3\langle y\rangle_n x_n y_n - 3\langle z\rangle_n x_n z_n \Big\}$$

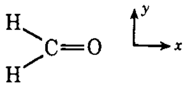
$$\Omega_{xyy} = -|e| \sum_n \Big\{ \langle x\rangle_n \Big(2y_n{}^2 - \frac{3}{2}x_n{}^2 - \frac{1}{2}z_n{}^2\Big) + 4\langle y\rangle_n x_n y_n - \langle z\rangle_n x_n z_n \Big\} \qquad (26)$$

$$\Omega_{xyz} = -\frac{5}{2}|e| \sum_n \{ \langle z\rangle_n x_n y_n + \langle x\rangle_n y_n z_n + \langle y\rangle_n z_n x_n \}$$

It is interesting to note that the methods developed here to evaluate molecular dipole and quadrupole moments by summing over atom dipole terms can also be applied to the estimation of higher order multipole moments. For instance, the molecular octapole moments are given in terms of the atom dipoles by[9] eq 26 where we have set the atom quadrupole and atom octapole moments to zero. We have used eq 26 and the atom dipole of Table II to evalute the octapole moments [in units of 10^{-34}(esu cm³)] for several molecules and compared our results with previous calculations. We obtain the following results for water, formaldehyde, and methane.



$\Omega_{xxx} = -2.3$
$\Omega_{xyy} = +4.4$
$\Omega_{xzz} = -2.1$



$\Omega_{xxx} = -1.5$
$\Omega_{xyy} = -0.7$
$\Omega_{xzz} = +2.2$

CH_4 $\Omega_{xyz} = +4.4$

These results can be compared to the literature results for water[21] $\Omega_{xxx} = -1.3$, $\Omega_{xyy} = +2.3$, $\Omega_{xzz} = -1.0$; for formaldehyde[22] $\Omega_{xxx} = -0.58$, $\Omega_{xyz} = -1.98$, $\Omega_{xzz} = +2.56$; and for methane $\Omega_{xyz} = +4.5$.[23]

The results in Table V are even better than results on molecular moments, since uncertainties in atom dipoles will introduce relatively small errors in the second moments of electronic charge. Deviations in second moments calculated with eq 22 are estimated to be 0.1–1.0 Å², which will produce deviations in the diamagnetic susceptibility of about 0–8 × 10^{-6} erg/(G² mol). The values of the diagonal elements of the diamagnetic susceptibility tensor combined with the diagonal elements of the paramagnetic susceptibility (available from the molecular g values) allows a determination of the total susceptibility elements as well as the bulk susceptibilities.[8]

In summary, we propose a method of evaluating (predicting) molecular electric dipole and quadrupole moments by summing over atomic dipole moments.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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(18) R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **51**, 3087 (1969).

(19) J. M. Schulman and G. J. Fizanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(20) T. D. Gierke, S. L. Hsu, and W. H. Flygare, *J. Mol. Spectrosc.*, **40**, 328 (1971). In this work a different value had been assigned to the atom dipole of an sp³ carbon bonded to an sp² carbon, which gave the opposite polarization in propene. Further investigation led us to the present choice of this atom dipole (see Table II).

(21) D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968).

(22) D. B. Neumann and J. W. Moscowitz, *ibid.*, **50**, 2216 (1969).

(23) D. E. Stogryn and A. P. Stogryn, *Mol. Phys.*, **11**, 371 (1966).