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Molecular Dipole Polarizabilities Based on MINDO/1 and MINDO/2 Wavefunctions*

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Molecular dipole polarizability values are derived from a MINDO/1 – and MINDO/2 – "finite perturbation treatment". The results are, especially in the MINDO/1 case, surprisingly good.

Introduction

The "finite perturbation theory" independently developed by Cohen and Roothaan [1] and by us [2–5], and subsequently given this name by Pople *et al.* [6], provided an exceptional stimulus to the calculation of second and higher order properties (dipole [1–5, 7–19] and quadrupole [10, 13] polarizabilities, susceptibilities [20], shielding [20] and coupling [21–25] constants, hyperpolarizabilities [5, 8, 10, 11, 26], and transition polarizabilities [27]). Since this theory, when applied at the CNDO/2 level [28], gives values for molecular dipole polarizabilities which are too low, we tested two other valence electron methods, MINDO/1 and MINDO/2 [29], for the same purpose. Is is the aim of this note to point out the unexpected result that these methods give much better results than the CNDO/2 method.

Method

Restricting ourselves for the present objective to the diagonal components α_{ii} of the molecular polarizability, we may describe the field dependence of the molecular dipole moment by [30]

$$\mu_i = \mu_i^{(0)} + \alpha_{ii} F_i + \cdots, i = x, y, z \qquad (1)$$

where μ_i and $\mu_i^{(0)}$ are the i-components of the total and permanent dipole moment, respectively, and F_i the strength of the uniform electric field applied in the i-direction. In order to incorporate F_i into the Hamiltonian operator, we have to add to the core matrix $\boldsymbol{H}^c$ the field dependent matrix $\boldsymbol{F}$, whose elements are the same for all of the three above mentioned valence electron procedures and which have been listed previously [17] [1]. For several values of F_i, values of μ_i are computed, and α_{ii} is obtained using the method of least squares to express μ_i according to (1) as a power series in F_i.

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* Part 15 of Properties of molecules in electric fields. Part 14: Schweig, A.: Angew. Chem., (in press).

[1] Some of the formulae in [17] are presented incorrectly and should be applied with caution.

Results and Discussion

Tables 1–3 list the calculated MINDO/1, MINDO/2 and CNDO/2[2] polarizabilities (Table 1 the α_{zz}, Table 2 the α_{xx} and α_{yy} components and Table 3 the mean polarizabilities $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$) together with previously calculated or experimental values. The orientation of molecules relative to the Cartesian coordinate system indicated in the Tables is chosen so that the coordinate axes and the principal polarizability axes coincide.

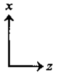
The Tables reveal two interesting results:

1) The quality of the calculated values clearly increases in the series: CNDO/2→MINDO/2→MINDO/1. This result is surprising, since previous experience [54] has shown MINDO dipole moments to be inferior to those calculated by CNDO/2.

2) Whereas MINDO polarizabilities of linear molecules along the molecular axis (α_{zz}) generally agree well with the experimental values, the polarizabilities perpendicular to the axis (α_{xx}) are much too low. A similar situation prevails in planar molecules (H_2O, C_2H_4) where the MINDO polarizabilities in the molecular plane (α_{zz} and α_{xx}) are much better (especially in the MINDO/1 case) than the polarizability perpendicular to the plane, (α_{yy}) being again much too low.

These results show that the semiempirical MINDO- "finite perturbation method" represents a practical combination of methods for predicting satisfactory numerical values of molecular polarizabilities along the axis for linear molecules and in the plane for planar systems. However, if equally good polarizabilities perpendicular to the molecular axis (linear molecules) or molecular plane are needed, the inclusion of some sort of polarization functions in the semiemperical method seems to be unavoidable.

Table 1. Polarizability component α_{zz} (in 10^{-24} cm^3)

 Molecule[a]	MINDO/1	MINDO/2	CNDO/2	Calculated	Experimental[b]
H – H	1.02	0.47	0.455 [17]	0.971 [13] 0.945 [32] 0.21 [33] 1.293 [34] 1.92 [35] 1.664 [36]	1.028 [49] 0.934 [50]
N ≡ N	2.79	2.78	1.153 [17]	1.10 [33] 4.67 [34] 3.84 [35] 5.746 [36] 1.56 [38]	2.23_1 [49] 2.38 [50]
F – F	2.25	—	0.936 [17]	1.904 [36] 2.248 [37] 1.08 [38] 2.15 [39]	

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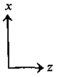
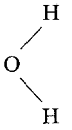
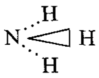
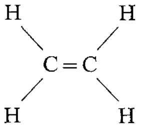
[2] All CNDO/2 polarizability values have been recalculated by us. In case of large discrepancies between our values and those of Hush and Williams, both values are listed in the Tables.

Table 1 (Continued)

 Molecule[a]	MINDO/1	MINDO/2	CNDO/2	Calculated	Experimental[b]
C≡O	2.85	2.26	1.070 [17]	2.11 [13] 1.67 [13] 1.76 [13] 4.32 [34] 4.803 [36] 3.222 [37] 3.264 [40]	2.33_2 [49] 2.60 [50]
O=C=O	4.44	3.93	1.994 [17]		4.03 [49] 4.93 [51]
N=N=O	5.58	5.73	2.58	3.65 [13] 4.07 [13]	4.97 [49] 4.86 [50]
F–H	0.60	—	0.327 [31]	0.830 [16] 0.32 [33] 0.63 [33] 1.002 [37] 0.859 [39] 0.779 [41] 0.732 [42] 0.808 [42] 0.616 [43] 0.791 [45]	
	0.67	0.33	0.22 [31]	1.452 [40] 0.749 [40] 1.073 [41] 1.067 [41] 0.88 [43] 1.162 [44] 1.00 [45] 1.150 [46] 0.489 [46]	
	0.53	0.53	0.21 0.651 [31]	1.624 [41]	2.41 [49] 2.42 [50]
CH_4	1.64	1.05	0.65 [31]	2.30 [18] 2.58 [35] 3.176 [40] 1.889 [41]	2.60 [50] 2.62 [52]
H–C≡N	4.71	3.36	1.52 1.862 [31]	1.845 [40] 1.831 [47]	3.92 [50]
H–C≡C–H	5.09	3.86	2.121 [17]		4.73 [49] 5.12 [50]
	5.45	4.29	2.46	4.20 [16] 2.40 [33] 4.08 [33] 5.61 [48]	

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[a] Experimental bond lengths and angles are used.

[b] Optical polarizabilities unless otherwise specified.

Table 2. Polarizability components α_{xx} and α_{yy} (10^{-24} cm^3)

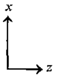
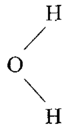
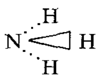
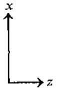
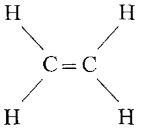
 Molecule[a]	MINDO/1	MINDO/2	CNDO/2	Calculated	Experimental[b]
H−H	0.00	0.00	0.000 [17]	0.678 [32] 0.00 [33] 0.801 [34] 0.24 [35] 0.572 [36]	0.714 [49] 0.718 [50]
N≡N	0.60	0.60	0.394 [17]	0.40 [33] 1.27 [34] 0.72 [35] 1.098 [36] 1.954 [37] 0.94 [38]	1.53_5 [49] 1.45 [50]
F−F	0.03	—	0.04 0.017 [17]	0.390 [36] 0.949 [37] 0.30 [38] 0.77 [39]	
C≡O	0.95	0.90	0.709 [17]	1.55 [34] 1.283 [36] 2.088 [37] 2.013 [40]	1.80_0 [49] 1.625 [50]
O=C=O	0.73	0.50	0.322 [17]		1.93 [49] 2.14 [51]
N=N=O	0.71	0.70	0.42		2.01 [49] 2.07 [50]
F−H	0.04	—	0.03 0.000 [31]	0.03 [33] 0.22 [33] 0.364 [34] 0.377 [36] 0.791 [37] 0.623 [39] 0.525 [41]	
	α_{xx} α_{yy}	α_{xx} α_{yy}	α_{xx} α_{yy}	α_{xx} α_{yy}	
	1.42 0.15	0.37 0.14	0.63 0.09 [31]	1.651 1.226 [40] 1.071 0.589 [40] 1.191 0.918 [41] 1.202 0.920 [41] 1.44 0.63 [43] 1.279 1.069 [44] 1.83 0.53 [45] 1.247 1.011 [46] 0.840 0.165 [46]	
	1.88	0.83	0.65 1.045 [31]	1.742 [41]	2.12 [49] 2.18 [50]

Table 2 (Continued)

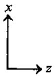
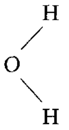
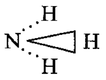
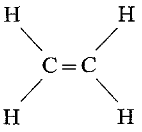
 Molecule	MINDO/1		MINDO/2		CNDO/2		Calculated		Experimental[b]
CH_4	1.64		1.05		0.65 [31]		2.30 [18] 2.58 [35] 3.176 [40] 1.889 [41]		2.60 [50] 2.62 [52]
$H-C\equiv N$	0.97		0.77		0.46 0.025 [31]		1.845 [40] 1.831 [47]		1.92 [50]
$H-C\equiv C-H$	0.73		0.54		0.33 0.000 [17]				2.87 [49] 2.43 [50]
	α_{xx}	α_{yy}	α_{xx}	α_{yy}	α_{xx}	α_{yy}	α_{xx}	α_{yy}	
	3.72	1.02	2.00	0.79	1.09	0.49	2.28 1.10 2.86 3.96	16 0.50 [33] 1.77 [33] 3.38 [48]	

[a] Experimental bond lengths and angles are used.
[b] Optical polarizabilities unless otherwise specified.

Table 3. Mean polarizability $\alpha(10^{-24}\ \text{cm}^3)$

 Molecule[a]	MINDO/1	MINDO/2	CNDO/2	Calculated	Experimental[b]
$H-H$	0.34	0.16	0.152 [17]	0.767 [32] 0.07 [33] 0.965 [34] 0.80 [35] 0.936 [36]	0.819 [49] 0.79 [50]
$N\equiv N$	1.33	1.33	0.647 [17]	0.63 [33] 2.40 [34] 1.76 [35] 2.648 [36] 2.651 [37] 1.15 [38]	1.76_7 [49] 1.76 [50]
$F-F$	0.77	—	0.339 0.323 [17]	0.895 [36] 1.382 [37] 0.56 [38] 1.23 [39]	
$C\equiv O$	1.58	1.35	0.829 [17]	2.44 [34] 2.283 [36] 2.466 [37]	1.97_7 [49] 1.95 [50] 1.94 1.98[c]

Table 3 (Continued)

 Molecule^{a}	MINDO/1	MINDO/2	CNDO/2	Calculated	Experimental^{b}
O=C=O	1.97	1.64	0.879 [17]	2.430 [40]	2.63 [49] 2.92 [51] 2.62 2.89^{c} 2.59 2.92^{c}
N=N=O	2.33	2.38	1.14		3.00 [49] 3.00 [50] 2.92 3.08^{c} 2.92 3.10^{c}
F–H	0.23	—	0.129 0.109 [31]	0.13 [33] 0.36 [33] 0.506 [34] 0.528 [36] 0.861 [37] 0.702 [39] 0.610 [41]	2.46 [44]
	0.75	0.28	0.32 [31]	1.443 [40] 0.803 [40] 1.061 [41] 1.063 [41] 0.98 [43] 1.170 [44] 1.12 [45] 1.136 [46] 0.489 [46]	1.49 [53] 1.46 1.49^{c}
	1.43	0.73	0.50 0.914 [31]	1.703 [41]	2.22 [49] 2.26 [50] 2.16 2.46^{c} 2.18 2.34^{c}
CH_4	1.64	1.05	0.65 [31]	2.30 [18] 2.58 [35] 3.176 [40] 1.889 [41]	2.60 [50] 2.62 [52] 2.57 2.59^{c} 2.54 2.62^{c}
H–C≡N	2.22	1.63	0.81 0.637 [31]	1.845 [40] 1.831 [47]	2.59 [50] 2.50 2.50^{c} 2.54 4.99^{c}
H–C≡C–H	2.18	1.65	0.927 0.707 [17]		3.49 [49] 3.33 [50] 3.40 3.91^{c} 3.45 3.96^{c}
	3.40	2.36	1.35	1.33 [33] 2.90 [33] 4.32 [48]	4.22 [49] 4.26 [50] 4.08 4.24^{c}

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[a] Experimental bond lengths and angles are used.

[b] Optical polarizabilities unless otherwise specified.

[c] Calculated from polarization values given in [50], the first value from the electronic polarization, the second from the total polarization (electronic + atomic polarization).

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