MINDO/3 Calculations of Molecular Electric Polarizabilities

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Summary A formalism is developed for calculating molecular electric polarizabilities by the MINDO/3 semiempirical SCF MO method, using finite perturbation theory; the results for a number of molecules agree well with experiment.

A number of papers have recently appeared[1-3] describing calculations of molecular polarizabilities by various methods. Here we report some preliminary results using an improved version (MINDO/3[4]) of the MINDO[5] semiempirical SCF MO method together with finite perturbation theory.[3,6]

The molecular polarizability tensor α_{ij} is defined by equation (1), where E is the total energy and F^i, F^j are

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial F^i \partial F^j}\bigg|_{\boldsymbol{F}\to 0} \qquad (1)$$

components of the electric field $\boldsymbol{F}$. For a closed-shell molecule, using the orbital approximation and the Hellmann–Feynman theorem, this becomes equation (2),[2]

$$\alpha_{ij} = -2\left[\frac{\partial}{\partial F^j}\sum_{k=1}^{N} < \psi_k^j \bigg| e\sum_m i_m \bigg| \psi_k^j > \right]_{F^j\to 0} \qquad (2)$$

where ψ_k^j is the kth MO calculated for a field F^j in the j direction, i_m is the i co-ordinate of electron m, and the sum is over the N occupied MOs. In the Roothaan approximation, this reduces to equation (3), where the sum is over the

$$\alpha_{ij} = \left[\sum_{\mu}\sum_{\nu}\frac{\partial P_{\mu\nu}^{j}}{\partial F^j} D_{\mu\nu}^{i}\right]_{F^j\to 0} \qquad (3)$$

basis set functions (μ, ν), $P_{\mu\nu}^j$ being the corresponding population density matrix element and $D_{\mu\nu}^i$ the dipole moment matrix element defined by equation (4).

$$D_{\mu\nu}^{i} = -\,\mathrm{e}< \mu \bigg| \sum_m i_m \bigg| \nu > \qquad (4)$$

In MINDO, which uses the same basic approximation as INDO,[7] the basis set functions are valence shell AOs of the atoms and matrix elements $D_{\mu\nu}^i$ are neglected if μ and ν are AOs of different atoms. The MINDO F matrix elements $F_{\mu\nu}$ in the presence of an electric field F are given by equation (5), where $F_{\mu\nu}^0$ is the matrix element in

$$F_{\mu\nu} = F_{\mu\nu}^{0} + \sum_i F^i D_{\mu\nu}^{i} \qquad (5)$$

the absence of an external electric field. The derivatives in equation (3) can be found quite easily by finite difference, assuming a small field δF^j and diagonalizing the corresponding F matrix [equation (5)] to get the perturbed orbital energies and hence the perturbed total energy. The one-centre dipole moment matrix elements $D_{\mu\nu}^i$ were calculated using Slater–Zener orbitals with the MINDO/3 values[4] for the orbital exponents.

The calculations were carried out for equilibrium geometries, these being found by minimising the total energy ($F = 0$) with respect to all geometrical variables.[8] Polarizabilities calculated in this way for a number of molecules are compared with experiment[9] in the table.

The agreement with experiment is generally good, especially for the larger molecules. Apart from H_2, it is as good as that given by any of the other procedures that have been tried.[1-4] The main source of error lies in the failure of MINDO/3 to reproduce atomic polarizabilities. This is due to the use of a minimum basis set without polarization functions (*cf.* ref. 3).

Thus the calculated polarizabilities of linear molecules in

TABLE. Calculated MINDO/3 results of the molecular polarizabilities

Molecule	Polarizability component	Calculated (10^{-24} cm^3)	Experimental (10^{-24} cm^3)
H_2	α_{zz}	0·76	0·93
N_2	α_{zz}	2·41	2·38
Cl_2	α_{zz}	5·30	6·60
O_2	α_{zz}	1·70	2·35
HF	α_{zz}	0·83	0·96
HCl	α_{zz}	1·80	3·13
CO	α_{zz}	2·17	2·60
HCN	α_{zz}	3·77	3·92
CO	α_{zz}	3·65	4·01
C_2H_2	α_{zz}	4·30	5·12
NCCN	α_{zz}	8·84	7·76
NH_3	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}{}^{a}$	1·18, 1·18, 0·43	2·18, 2·18, 2·42
CH_4	$\alpha_{xx}\ (=\alpha_{yy}, =\alpha_{zz})$	1·26	2·60
MeCl	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}{}^{a}$	1·32, 1·32, 3·50	4·14, 4·14, 5·40
Benzene	$\alpha_{xx}\ (=\alpha_{yy})$	10·03	12·31
Pyridine	$\alpha_{xx}, \alpha_{yy}{}^{b}$	14·52, 10·52	11·88, 10·84
Chlorobenzene ..	$\alpha_{xx}, \alpha_{yy}{}^{b}$	10·20, 14·37	13·24, 15·93
o-Dichlorobenzene ..	$\alpha_{xx}. \alpha_{yy}{}^{b}$	12·79, 15·83	14·31, 18·68
m-Dichlorobenzene ..	$\alpha_{xx}, \alpha_{yy}{}^{b}$	16·98, 12·17	17·71, 16·57
p-Dichlorobenzene ..	$\alpha_{xx}, \alpha_{yy}{}^{b}$	10·26, 18·92	12·48, 21·29
Toluene	$\alpha_{xx}, \alpha_{yy}{}^{b}$	12·85, 14·96	13·66, 15·64

[a] Symmetry axis. [b] $\mu = \mu_y$.

directions perpendicular to the molecular axes, and of planar molecules perpendicular to the molecular planes, are close to zero, which of course is incorrect.

The results reported here nevertheless seem very encouraging, particularly since the calculations can be carried out quickly even for quite large molecules. Thus only a few seconds are needed to calculate (CDC 6600) the polarizability of dichlorobenzene, if the geometry is assumed, while a complete calculation of the geometry of such a molecule takes only 5 min. The contrast with *ab initio* methods is the more intriguing given that MINDO/3 seems to give rather better results.

No problems should arise in the extension of these calculations to hyperpolarizabilities; work in that direction is in progress.

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