Calculation of Polarizabilities by the CNDO Method

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The polarizabilities of a number of small and medium size molecules are calculated using CNDO/2 wave functions. The first-order and the second-order perturbation equations are solved by variational procedures. The results are encouraging for the component along the internuclear axes and in the molecular plane. The effect of deorthogonalization of the CNDO/2 orbitals is discussed.

Key words: Polarizabilities, CNDO calculation of ~

1. Introduction

The electric polarizability is a most important molecular property. It determines the interaction forces in gases and liquids, the stability and charge transfer properties of molecular crystals, and through its derivatives the non-resonance Raman intensities. Until now very few *ab initio* calculations have been reported for polarizabilities and with only partial success. Only recently, an *ab initio* calculation [1], using a large basis set, has produced very accurate results for the polarizabilities of some small molecules. However the complexity of these calculations is too great for applications to larger molecules.

Naturally, the attention is focussed on semi-empirical calculations, and several authors [2–5] have performed polarizability calculations within the CNDO approximation. However, the calculated values of the polarizabilities are generally much too small in comparison with the experimental ones. This is the more disappointing as the CNDO scheme is very successful in the calculation of dipole moments. The different methods are of variational perturbation nature and are very sensitive to the zero-order wave function. This is of course very unfortunate since we are working with a very crude ground state wave function in the CNDO approximation.

Recently [6] we proposed a variational scheme, which through the solution of both the first- and the second-order perturbation equation should prove more insensitive to the quality of the ground state wave function. The perturbation equations are both solved through a variational procedure. In Sect. 2 of this paper we give a brief summary of the theory and discuss the choice of variational functions. Also the question of how to calculate the matrix elements over the electric field operator in the CNDO approximations is discussed in this section of the paper. The numerical results are given in Sect. 3, where they are also compared with the values obtained by different methods of CNDO calculations. The results of the paper are summed up in Sect. 4, where we also discuss the possibilities of further improvements.

2. Theory

We consider a molecular system which is represented by a Hamiltonian H having a set of eigenvalues ε_n and corresponding eigenfunctions ψ_n. The exact second-order perturbation energy due to a perturbation V is then defined by

$$\varepsilon_{0,2} = - \sum_{n \neq 0} \frac{\langle \psi_0 \mid V \mid \psi_n \rangle \langle \psi_n \mid V \mid \psi_0 \rangle}{\varepsilon_n - \varepsilon_0} \tag{1}$$

Our calculations are based on an approximate molecular wave function φ_0, which has an error represented by a parameter λ_0

$$\varphi_0 = \mu_0 \psi_0 + \lambda_0 \chi \tag{2}$$

We consider the perturbation equation

$$(H - E_0)\varphi_0' + (V - E_0')\varphi_0 = 0$$
$$E_0 = \langle \varphi_0 \mid H \mid \varphi_0 \rangle \tag{3}$$

An approximate solution f_0 to this equation may be obtained by minimizing the expression

$$A = \langle f \mid H - E_0 \mid f \rangle + \langle f \mid V \mid \varphi_0 \rangle + \langle \varphi_0 \mid V \mid f \rangle \tag{4}$$

with respect to a variational function f.

Recently [6] we determined the magnitude of errors contained in various theoretical methods, and we found that the difference between A and $\varepsilon_{0,2}$ is linear in the parameter λ_0 and quadratic in the parameter λ_1, the latter parameter representing the error in the function f_0. We call A a first-order approximation to $\varepsilon_{0,2}$.

Since we are working with highly approximate wave functions the error linear in λ_0 is very unfortunate. A more accurate theoretical result may be obtained by considering the second-order perturbation equation

$$(H - E_0)f_0' + (V - E_0')f_0 = E_0''\varphi_0 \tag{5}$$

An approximate solution to f_0' is found by minimizing the expression

$$\langle g \mid H - E_0 \mid g \rangle + \langle g \mid V - E_0' \mid f_0 \rangle + \langle f_0 \mid V - E_0' \mid g \rangle \tag{6}$$

with respect to the variational function g. In this way we can avoid the error linear in λ_0 since we showed [6]

$$\varepsilon_{0,2} = A + \langle g_0 \mid H - E_0 \mid \varphi_0 \rangle + \langle \varphi_0 \mid H - E_0 \mid g_0 \rangle + O(\lambda_0^2, \lambda_1^2, \lambda_2^2) \tag{7}$$

where g_0 is the approximate solution to Eq. (6), and λ_2 represents the error in this function. We take Eq. (7) as the second-order approximation to $\varepsilon_{0,2}$. The above results are valid only if the variational functions f and g fulfill the requirement

$$\langle f \mid \varphi_0 \rangle + \langle g \mid \varphi_0 \rangle = 0 \tag{8}$$

In this calculation we take for the ground state wave function φ_0, a single determinant of molecular orbitals as determined by the LCAO SCF method in the zero differential approximation. We use the original CNDO/2 parametrization as proposed by Pople *et al.* [7].

The variational function f is taken to be

$$f = \sum_{i=1}^{N} c_i \, {}^i\theta_k^l \tag{9}$$

where θ_k^l is the determinantal wave function obtained by moving one electron from an occupied molecular orbital, k, to an unoccupied one, l. Substitution of Eq. (9) into Eq. (4) and subsequent differentiation leads to the following system of simultaneous linear equations

$$\sum_i c_i (H_{ki} - E\Delta_{ki}) + V_{k0} = 0, \quad k = 1, 2, \ldots, N \tag{10}$$

where

$$\begin{aligned}
H_{ki} &= \langle {}^k\theta \mid H - E_0 \mid {}^i\theta \rangle \\
\Delta_{ki} &= \langle {}^k\theta \mid {}^i\theta \rangle \\
V_{k0} &= \langle {}^k\theta \mid V \mid \varphi_0 \rangle
\end{aligned} \tag{11}$$

Substitution of the solution to Eq. (10), $\{c_i^0\}$, back into Eq. (4) gives the result for A at the minimum.

$$A = \sum_i c_i^0 V_{i0} \tag{12}$$

In a similar way we choose the variational function g to be

$$g = \sum_{i=1}^{M} d_i \, {}^i\Pi_{kl}^{mn} \tag{13}$$

where Π_{kl}^{mn} is the determinant wave function obtained by moving two electrons from the occupied molecular orbitals k and l to the unoccupied ones m and n. Substitution of this expression for g into Eq. (6) leads again to a system of simultaneous linear equations.

$$\sum_i d_i (H_{ki} - E_0 \Delta_{ki}) + V_{kf0} = 0, \quad k = 1, 2, \ldots, M \tag{14}$$

where

$$H_{ki} = \langle {}^k\Pi \mid H - E_0 \mid {}^i\Pi \rangle$$

$$\Delta_{ki} = \langle {}^k\Pi \mid {}^i\Pi \rangle$$

$$V_{kf_0} = \langle {}^k\Pi \mid V \mid f_0 \rangle = \sum_{j=1}^{N} c_j^0 \langle {}^k\Pi \mid V \mid {}^j\theta \rangle \tag{15}$$

In order to make a systematic choice of the variational functions g and f, all singly and doubly excited states were included in the calculation. The above choice of variational functions fulfils automatically the orthogonality requirement of Eq. (8), and it also has calculational advantages due to the orthogonality of the molecular orbitals. By this choice we also keep the same orbital exponents for the functions f and g as for the ground state function. This is in accordance with some calculations on small molecules performed with the same method [8].

The integrals over the molecular Hamiltonian and the overlap integrals are all calculated within the same CNDO/2 approximation as is used to determine the ground state wave function. In most calculations [3, 5] of polarizabilities in CNDO approximation only one-center integrals are retained in the matrix elements over the electric field perturbation operator V. However, we think it is more consistent to include the two-center integrals also. The MOs resulting from a CNDO/2 calculation may be interpreted [9, 10] as linear combinations of orthogonal AOs λ. They are connected with the Slater AOs χ through the Löwdin transformation [10]

$$\lambda = \chi S^{-1/2} \tag{16}$$

where S is the overlap matrix in χ basis. Instead of using the coefficient matrix C, arising from the solution of Roothaan's equations, we applied the matrix $C' = S^{-1/2}C$ in a rigorous calculation of matrix elements over the operator V. This procedure is denoted by CNDO/2D.

3. Results and Discussion

In all the calculations the geometries of the molecules followed the data listed in Ref. [11]. The z direction is along the principal axis, the y axis perpendicular to the molecular plane. The results of the calculations for the acetylene molecule is shown in Table 1. From the table it is seen that the CNDO/2D values are much better than

Table 1. Polarizabilities of C_2H_2 (10^{-24} cm^3)

Comp.	CNDO/2		CNDO/2D		Experimental	
	$V-1$[a]	$V-2$[b]	$V-1$	$V-1$	[12]	[13]
α_{zz}	2.46	3.34	3.72	4.95	4.73	5.12
α_{xx}	0.327	0.325	0.369	0.368	2.87	2.43

[a] Calculated from the first-order variational equation (4).
[b] Calculated from the second-order variational equation (6).

the CNDO/2 ones. This is in agreement with the findings of Shillady *et al.* [14], who investigated the effect of de-orthgonalization of the CNDO/2 orbitals by a Löwdin transformation in the calculation of dipole moments. The value obtained for the z component by solving the first-order equation only, is still too low. However, the correction term, calculated from the solution of the second-order equation, brings the value close to the experimental one. The x component is much too low for both the first- and the second-order approximation to $\varepsilon_{0,2}$. The reason of this is not so much a consequence of the semiempirical approximations, but rather that the calculations are performed with a minimum basis set. This restricts the electrons to be shifted mainly along the bonds. In order to allow for a vertical shift it is necessary to introduce polarization functions [17].

Table 2. Polarizability component α_{zz} of linear molecules (10^{-24} cm^3)

Molecule	$V-1$[a]	$V-2$[b]	FPT[c]	PS[d]	PSD[e]	Experimental [12]	[13]
N_2	1.87	2.85	1.15	1.47	0.77	2.23	2.38
CO	1.70	2.46	1.07	1.37	0.87	2.33	2.60
CO_2	2.96	4.58	1.99	2.89	—	4.03	4.93
N_2O	4.14	6.52	2.58	—	—	4.97	4.86
HCN	2.70	3.85	1.52	—	—	3.92	—
C_2H_2	3.72	4.95	2.12	2.43	1.54	4.73	5.12

[a] and [b] see Table 1.
[c] Calculated from finite perturbation theory [2].
[d] Calculated from Eq. (1) using CI with singly excited configurations [5].
[e] Calculated from Eq. (1) using CI with singly and doubly excited configurations [4].

The values of the parallel component of the polarizability for a series of linear molecules are given in Table 2. Here we also show the values obtained using different approaches within the CNDO approximation. In the finite perturbation theory (FPT), developed by Cohen and Roothaan [15], the SCF MO semi-empirical equations are solved for the molecule in the absence and presence of an external electric field. The calculations are repeated for various strengths of the applied field and the polarizability is determined from the quadratic term in the Taylor expansion of the energy. The values in the two next columns shown are obtained from a direct application of the perturbation equation (1) with a CNDO-CI wave function substituted for the exact one. In the column denoted PS, only singly excited states are included in the CI calculation [5], whereas in the column denoted PSD, both singly and doubly excited configurations are included [4]. Again our values agree generally well with the experimental ones, while the values from the other calculations are too small. It is interesting to note that these values are smaller than the values obtained by solving the first-order equation only. It should be noted that the same amount of work is needed in solving the first-order equation as in solving the singly excited CI equations, since both sets of equations involve the same matrix elements. The same can be said about the second-order equation and the CI

treatment including both singly and doubly excited states. The values in Table 2 were determined using the CNDO/2D method. We also performed single-center CNDO/2 calculations but the values followed those from acetylene, being too small. Also the perpendicular component turned out to be too small.

In Table 3 we show the results of some calculations on non-linear molecules. Only for C_2H_4 the PSD values are available. They are 1.96, 0.98, 0.45 for α_{zz}, α_{xx} and α_{yy} respectively. The values obtained with the proposed variational method are better than the ones from the other CNDO calculations, but generally they are too small. However, the components in the molecular plane agree quite well with the experimental values, in particular, the benzene calculation is encouraging. In this calculation we limited the number of doubly excited states by the requirement that the matrix element $V_{kf_0} \geqslant 1$ a.u. Thereby the number of doubly excited states was reduced from 669 to 137. The above restriction was tested on C_2H_6 and only led to a change from 3.21 to 3.19 in the value of the parallel component of the polarizability.

4. Concluding Remarks

By solving the first-order perturbation equation through a variational procedure we obtain values which are better compared with other CNDO methods. However, the values are still too low. The correction term obtained from a solution of the second-order equation brings the values close to the experimental ones. These remarks only apply to the parallel component of the polarizability, the perpendicular being still much too small.

Table 3. Polarizability components of non-linear molecules (10^{-24} cm^3). The z direction is along the principal axis, and the y axis perpendicular to the molecular plane

Molecule	Comp.	$V-1$[a]	$V-2$[b]	FPT[c]	PS[d]	Experimental [12]	
NH$_3$	α_{zz}	0.33	0.40	0.21	0.23	2.41	
	α_{xx}	1.35	1.50	0.65	0.70	2.12	
CH$_4$	α_{zz}	1.32	1.48	0.65	0.64	2.60	
	α_{zz}	0.55	0.68	0.22	—	1.45[f]	
H$_2$O	α_{xx}	1.14	1.24	0.63	—	1.65	
	a_{yy}	0.01	0.01	0.09	–	1.23	
	α_{zz}	2.23	3.10	—	—	4.55[e]	2.49[f]
HCO$_2$	α_{xx}	1.66	1.89	—	—	2.70	1.84
	α_{yy}	0.45	0.45	—	—	2.31	0.73
	α_{zz}	3.76	4.71	2.46	2.75	5.7[f]	
C$_2$H$_4$	α_{xx}	2.73	3.19	1.09	1.25	5.15	
	α_{yy}	0.46	0.45	0.49	0.48	1.46	
C$_2$H$_6$	α_{zz}	2.26	2.42	—	1.40	3.98	
	α_{xx}	2.78	3.21	—	1.32	5.49	
C$_6$H$_6$	α_{zz}	9.49	12.20	—	—	12.30	

[a, b, c] and [d] see Tables 1 and 2.
[e] *Ab initio*, from Ref. [1].   [f] CNDO extended basis, [3].

It is shown that calculations of matrix elements over the electric field operator, using Löwdin orthogonalized orbitals, lead to better values than calculations where only the one-center contribution is included.

In order to calculate the two important quantities, the mean value of the polarizability and the anisotropy, it is absolutely necessary to improve the values of the perpendicular components also. One possibility is to work with different semi-empirical approximations. This has been done using finite perturbation theory and MINDO wave functions [2, 16], and using CNDO/S [4] wave functions with the perturbation equation (1) [4]. Even though the MINDO/1 [2] and the MINDO/3 [16] calculations give better results than the corresponding CNDO/2 calculations for the parallel component, the values of perpendicular components are still much too low. The most efficient way to improve the calculations is probably to introduce some kind of polarization functions [17] in the basis set in order to improve the perturbed functions f and g. Calculations with extended basis sets in the CNDO approximation [3, 5] support this idea, and we are currently engaged in such calculations.

References

1. Meyer, W., Werner, W. J.: Mol. Phys. **31**, 855 (1976)
2. Meyer, H., Schweig, A.: Theoret. Chim. Acta (Berl.) **29**, 375 (1972)
3. Teixeira-Dias, J. J. C., Sarre, P. J.: Proc. Roy. Soc. **A264**, 906 (1975)
4. Miyazaki, T., Shinoda, H.: Bull. Chem. Soc. Japan **46**, 1216 (1973)
5. Shinoda, H., Akutagawa, T.: Bull. Chem. Soc. Japan **48**, 3431 (1975)
6. Hameka, H. F., Svendsen, E. Nørby: Intern. J. Quantum Chem. **10**, 249 (1976)
7. Pople, J. A., Santry, D. P., Segal, G. A.: J. Chem. Phys. **43**, S129 (1965)
8. Svendsen, E. Nørby, Hameka, H. F.: J. Chem. Phys. **62**, 2760 (1975)
9. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
10. Löwdin, P. O.: J. Chem. Phys. **18**, 365 (1950)
11. Tables of interatomic distances and configurations in molecules and ions. London: The Chemical Society 1958, and its supplement (1965)
12. Bridge, N. J., Buckingham, A. D.: Proc. Roy. Soc. **A295**, 334 (1966)
13. Landolt-Börnstein, A. D.: Zahlenwerte und Funktionen, Vol. 1, Part 3. Berlin: Springer 1951
14. Shillady, D. D., Billingsley, F. P.: Theoret. Chim. Acta (Berl.) **21**, 1 (1971)
15. Cohen, H. D., Roothaan, C. C. J.: J. Chem. Phys. **43**, 534 (1965)
16. Dewar, J. S. H., Haddon, R. C., Suck, S. H.: J. Chem. Soc. Chem. Commun. **43**, 611 (1974)
17. Teixeira-Dias, J. J. C., Murrell, J. N.: Mol. Phys. **19**, 329 (1970)