Theoret. Chim. Acta (Berl.) 45, 241–247

THEORETICA CHIMICA ACTA

The Calculation of Ground and Excited State Molecular Polarizabilities: A Simple Perturbation Treatment

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Second order perturbation theory has been coupled with the CNDO/S CI method of Del Bene and Jaffé to calculate the ground and excited state polarizabilities of various molecules. It is found that this treatment produces reasonably good polarizabilities with great computational ease.

Key words: Excited state molecular polarizabilities

1. Introduction

Within recent years the calculation of molecular polarizabilities by means of wave mechanics has received widespread attention [1–15]. Unfortunately, the efficiency, economy, and practicability of many proposed techniques are open to question. Therefore, in the *spirit* of the CNDO/S CI formalism as developed by Del Bene and Jaffé [16], we have attempted a coupling of simple perturbation theory with this semiempirical method. It was hoped that we could predict the static molecular polarizabilities of both ground and excited states with reasonable accuracy and relative computational ease.

2. Theory and Method

Second order perturbation theory may be utilized to derive a general relation for the static polarizability of any molecular state [17]. The polarizability tensor α^n of a state n may be written in the following form.

$$\alpha^n = 2e^2 \sum_{m(\neq n)} \frac{\left\langle \Psi_n^0 \middle| \sum_i r_i \middle| \Psi_m^0 \right\rangle \left\langle \Psi_m^0 \middle| \sum_i r_i \middle| \Psi_n^0 \right\rangle}{E_m^0 - E_n^0} \tag{1}$$

Table 1. Ground state polarizabilities[a]

	This work[b]							Other calculations						Experimental values				
Molecule	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	α_{xy}	α_{xz}	α_{yz}	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	Method	Ref.	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	Ref.
CO	1.31	2.44	1.31	1.68				0.95	2.85	0.95	1.58	MINDO/1-FPT	10	1.62	2.60	1.62	1.95	19
								0.90	2.26	0.90	1.35	MINDO/2-FPT	10	1.80	2.33	1.80	1.98	20
								0.71	1.07	0.71	0.83	CNDO/2-FPT	7					
								1.14	3.70	1.14	1.99	CNDO/2-Variational	11					
CO_2	0.51	6.38	0.51	2.46				0.73	4.44	0.73	1.97	MINDO/1-FPT	10	1.93	4.03	1.93	2.63	20
								0.50	3.93	0.50	1.64	MINDO/2-FPT	10					
								0.32	1.99	0.32	0.88	CNDO/2-FPT	7					
								1.34	6.45	1.34	3.04	CNDO/2-Variational	11					
CH_4	1.13	1.13	1.13	1.13				1.64	1.64	1.64	1.64	MINDO/1-FPT	10	2.62	2.62	2.62	2.62	19
								1.05	1.05	1.05	1.05	MINDO/2-FPT	10					
								0.65	0.65	0.65	0.65	CNDO/2-FPT	7					
								3.10	3.10	3.10	3.10	CNDO/2-Variational-Perturbation	11					
C_2H_6	1.97	2.34	2.34	2.21				5.68	5.84	5.84	5.79	CNDO/2-Variational	11	5.49	3.98	3.98	4.48	19
								1.32	1.21	1.21	1.24	CNDO/2-FPT	11					
C_4H_8 (Trans)	3.91	19.49	1.37	8.22														
C_4H_{10}	2.62	3.41	2.44	2.82														
C_2H_2	0.70	6.44	0.70	2.62				0.73	5.09	0.73	2.18	MINDO/1-FPT	10	2.87	4.73	2.87	3.49	20
								0.54	3.86	0.54	1.65	MINDO/2-FPT	10					
								0.33	2.12	0.33	0.71	CNDO/2-FPT	7					
C_2H_4	2.18	7.29	1.05	3.51				3.72	5.45	1.02	3.40	MINDO/1-FPT	10				4.22	20
								2.00	4.29	0.79	2.36	MINDO/2-FPT	10					
								1.09	2.46	0.49	1.35	CNDO/2-FPT	10					

H_2CO	1.19	3.47	0.66	1.77				2.29	4.28	1.71	2.76	CNDO/2-Variational	11	2.76	2.76	1.83	2.45	19
								0.66	1.48	0.66	0.93	CNDO/2-FPT	11					
HFCO	1.67	2.95	0.67	1.76														
F_2CO	1.46	3.51	0.62	1.88														
HCOOH	2.11	3.79	0.75	2.22														
CH_3CHO	3.12	4.30	1.82	3.09	1.18	0.00	0.00	4.71	6.76	3.94	5.14	CNDO/2-Variational	11				4.59	19
								1.30	2.14	0.99	1.48	CNDO/2-FPT	11					
$(CH_3)_2CO$	3.11	5.07	2.50	3.56				7.08	9.95	6.34	7.79	CNDO/2-Variational	11	4.88	7.14	7.16	6.39	19
								1.96	3.17	1.56	0.93	CNDO/2-Variational	11					
$(CH_3)_2O$	2.50	2.33	2.18	2.33				5.45	6.13	5.28	5.62	CNDO/2-Variational	11	4.39	6.38	4.94	5.24	19
								1.28	1.96	1.18	1.47	CNDO/2-FPT	11					
Benzene	13.19	13.50	0.90	9.20				10.7	10.7	1.68	7.69	CNDO/S-FPT	23	11.1	11.1	7.4	9.87	20
Naphthalene	20.14	33.07	0.68	17.96				16.3	22.6	2.90	13.9	CNDO/S-FPT	15	17.6	10.3	21.5	16.5	21
Anthracene	65.54	34.64	0.12	33.43				40.3	26.7	4.10	23.7	CNDO/S-FPT	23	35.9	24.5	15.9	25.4	22
Phenanthrene	73.61	36.64	0.27	36.84				30	18			PI-FPT	4					
Pyridine	12.16	12.82	1.02	8.67														
Pyrimidine	11.86	12.16	1.58	8.53														
Pyridazine	13.32	12.73	1.76	9.27														
Pyrazine	12.06	13.34	1.14	8.85														
Phenol	13.42	15.20	1.21	9.94	0.00	0.06	0.00											
Toluene	13.27	14.45	1.08	9.60	0.00	0.12	0.00											

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[a] Units, 10^{-24} cm^3.

[b] Maximum of 60 configurations used.

[c] FPT—Finite Perturbation Theory.

Here it is expressed in terms of the transition moment integrals between states m and n, which are described by the eigenfunctions Ψ_m^0, Ψ_n^0 with eigenvalues E_m^0, E_n^0, respectively [18].

This equation may also be stated in terms of the polarizability tensor components $\alpha_{\mu\nu}^n$,

$$\alpha_{\mu\nu}^n = 2e^2 \sum_{m(\neq n)} \frac{\left\langle \Psi_n^0 \middle| \sum_i r_{\mu i} \middle| \Psi_m^0 \right\rangle \left\langle \Psi_m^0 \middle| \sum_i r_{\nu i} \middle| \Psi_n^0 \right\rangle}{E_m^0 - E_n^0} \tag{2}$$

where $r_{\mu i}$ is the $\mu(\mu, \nu = x, y, z)$ component of the vector r_i.

The actual evaluation of expression (2) can be readily accomplished within the CNDO/S CI formalism [16], subject to the following constraints:

1. The CNDO/S CI wavefunctions are substituted directly for the exact zero order wavefunction.
2. The summation over all states m involves only singly excited configurations, and generally must be truncated.

3. Results and Discussion

$\alpha_{\mu\nu}$, the components of the molecular polarizability, and the average polarizability $\bar{\alpha}$ (where $\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$) were calculated for a number of molecules. The results obtained for their ground state polarizabilities may be found in Tables 1 and 2. Table 3 contains calculated polarizabilities for the two lowest excited states of naphthalene. The polarizabilities for the ground and lowest excited states of azulene are found in Table 4. Also included in Tables 3 and 4 are the values for $\Delta\alpha_{\mu\mu}$, the difference in polarizability between ground and excited states.

Cursory analysis of Table 1 reveals that, for small molecules, our theoretically predicted ground state polarizabilities are lower than those found through experiment. There is favorable agreement in the cases of CO and CO_2, but this may well be fortuitous.

For aromatic molecules, the average polarizabilities $\bar{\alpha}$ agree quite well with experiment. Yet, α_{zz}, the out-of-plane polarization is found to be too small for all cases studied. This phenomenon has been observed by other investigators using

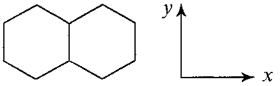
Table 2. Polarizabilities of benzene[a]

Number of Configurations	Polarizability component		
	α_{xx}	α_{yy}	α_{zz}
50	13.19	13.19	0.90
60	13.50	13.19	0.90
70	13.81	13.81	1.75

[a] Units, 10^{-24} cm^3.

Table 3. Excited state polarizabilities of naphthalene[a]

Naphthalene



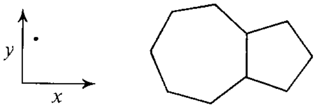
$^1B_{3u}$	This work	Ref. [15]	Exp. Ref. [23]	$^1B_{2u}$	This work	Ref. [15]	Exp. Ref. [23]
α_{xx}	42.8	29.2, 31.7		α_{xx}	131.5	57.8, 61.4	
α_{yy}	12.2	13.5, 14.8		α_{yy}	33.6	24.3, 23.7	
α_{zz}	1.1	3.7, 3.6		α_{zz}	1.2	3.7, 3.5	
$\bar{\alpha}$	18.7	15.5, 16.7		$\bar{\alpha}$	55.4	28.6, 29.5	
$\Delta\alpha_{xx}$	9.8	6.6, 9.1		$\Delta\alpha_{xx}$	98.5	35.2, 38.8	
$\Delta\alpha_{yy}$	7.9	−2.8, −1.5	−0.1±1.3	$\Delta\alpha_{yy}$	13.4	8.0, 7.4	9.5±7.9
$\Delta\alpha_{zz}$	0.4	0.8, 0.7		$\Delta\alpha_{zz}$	0.5	0.8, 0.6	
$\Delta\bar{\alpha}$	1.1	1.5, 2.8	+1.9±0.3	$\Delta\bar{\alpha}$	37.9	14.7, 15.6	9.8±1.6

[a] Units, 10^{-24} cm^3.

minimum basis sets [15], and is most likely due to the insufficiency of this basis, which allows for little migration of charge normal to the molecular plane.

The anisotropy of the results for benzene in Table 1 is disturbing. This can be shown, however, to be an artifact brought about by the truncation of the CI expansion, which in this case, accidentally occurred between a pair of degenerate configurations. If care is taken not to truncate in such a manner, the expected isotropy will be found, cf. Table 2. Further increase in the number of singly excited

Table 4. Ground and excited state polarizabilities for azulene[a]



	State				
	Ground			$^1B_1$	
Component	Exp[b]	This work	Ref. [24]	This work	Ref. [24]
α_{xx}		48.1	29.5	22.0	24.3
α_{yy}		25.0	17.0	12.0	17.0
α_{zz}		1.4	3.1	0.8	3.4
$\bar{\alpha}$		24.8	16.5	11.6	14.9
$\Delta\alpha_{xx}$	−3.5	−26.1	−5.2		
$\Delta\alpha_{yy}$		−13.0	0.0		
$\Delta\alpha_{zz}$		−0.6	0.3		
$\Delta\bar{\alpha}$		−13.2	−1.6		

[a] Units, 10^{-24} cm^3.
[b] Ref. [25].

configurations, to include all possible excitations, resulted in a marginal change in the out-of-plane polarizability and a small increase in the inplane components of the tensor. No quantitative relationship between the number of configurations in the CI expansion and the value of the polarizability components was found for benzene or other molecules tested (e.g. formaldehyde, pyridine).

If the results of various theoretical treatments are compared (Table 1), we find that this simple perturbation method produces ground state polarizabilities that are, in most cases, in reasonable agreement with experiment and, in many instances, of better quality than the polarizabilities produced elsewhere. In addition, whenever each Cartesian coordinate transforms in a different irreducible representation than every other coordinate, the perturbation treatment must produce vanishing off-diagonal polarizability components (as either transition moment integral vanishes (Eq. 2)). But in molecules of low symmetry, where this is not the case, the off-diagonal components are *readily* produced by this perturbation theory.

The comparison of theory and experiment for the $^1B_{3u}$ and $^1B_{2u}$ excited states of naphthalene (Table 3) seems to indicate that the predictions of Meyer, Schulte, and Schweig [15] are in better agreement with the experimental measurements of Mathies and Albrecht [23] than those predicted herein. It should be realized, however, that these experimental results are quite tenuous. Furthermore, the predictions of this simple perturbation method do parallel those of the German authors; and this fact is most encouraging.

In the case of azulene, this theory predicts all the polarizability components to be smaller in the excited state than in the ground state (Table 4); in other words, the polarizability change upon excitation is negative. This result correlates well with the finite perturbation treatment (FPT) of Schweig [24], and is in qualitative agreement with the experimental measurements of Marchetti [25], which indicate that the change in the long axis polarizability component is negative for the lowest $\pi\pi^*$ state of azulene.

We would finally like to comment on the relative ease of computation afforded by this perturbation method with a comparison to the FPT of Schweig *et al.*, a technique that employs a power series expansion of the dipole moment component for a molecule in an electric field. Since this latter method requires a minimum of seven calculations of the induced dipole moment for *each* polarizability component, it follows that at least twenty-one individual CI calculations must be performed for each state in question. This is in distinct contrast to our perturbation treatment which, in just one CNDO/S-CI calculation, provides all polarizability tensor components for all states included in the CI.

We have recently extended this technique to the calculation of triplet state polarizabilities. Again there is reasonably good agreement with the work of Schweig [15] as exemplified in the following results for the $^3B_{1u}$ state of naphthalene. We find the *xx*, *yy*, *zz* components to be 38.9, 8.5, and 1.1 ($\times 10^{-24}$ cm^3), respectively, while Schweig reports 38.4, 13.8, and 3.7 ($\times 10^{-24}$ cm^3).

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Received May 18, 1976/March 11, 1977