

Approximate Variation-Perturbation Calculations of the Second-Order Molecular Properties

II. Electric Polarizabilities

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The variation-perturbation technique is applied to the calculation of the electric polarizability tensor of diatomic molecules within the CNDO/2 approximation. The results obtained in this paper are similar to those found in the non-empirical variation-perturbation approach within the minimal STO basis set. They are also compared with other CNDO/2 calculations and with existing experimental data. It follows from this comparison that the CNDO/2 variation-perturbation method does not allow for the calculation of the polarizability anisotropies. On the other hand, the rotational average of the polarizability tensor can be predicted in agreement with both the experimental data and non-empirical results.

Das Variations-Störungsverfahren wird im Rahmen der CNDO/2-Näherung zur Berechnung von elektrischen Polarisierungstensen zweiatomiger Moleküle herangezogen. Die Resultate ähneln denen des analogen, aber auf ab initio-Rechnungen basierenden Verfahrens mit einem minimalen Satz von Slaterfunktionen. Es ergibt sich, daß die Berechnung der Anisotropien nicht möglich ist, wohl aber die der räumlichen Mittelwerte.

Introduction

Several attempts have been made to develop a reliable method for the evaluation of the electric polarizability tensor within the framework of semiempirical all-valence-electron theories. The perturbed Hartree-Fock theory [1, 2] simplified according to the CNDO/2 approximations of Pople *et al.* [3, 4] has been studied by Davies [5]. However, Davies concluded that the restriction imposed on the orbital basis set in the CNDO method does not allow for an adequate representation of the perturbed molecular orbitals. The components of the electric polarizability tensor calculated by Davies [5] were much too low.

A finite perturbation method for the solution of the unrestricted open-shell CNDO/2 equations in the presence of an external electric field has been adopted by Hush and Williams [6]. These authors have performed calculations of the electric polarizability for various linear molecules. According to their results, the average polarizabilities are considerably underpredicted whereas the calculated polarizability anisotropies are in substantial agreement with existing experimental data. These latter were even better predicted by the CNDO method than by the non-empirical calculations. More recently Hush and Williams [7] improved their results for the average polarizabilities by using a semiempirical correction scheme. In this way they obtained remarkably good results for both the average polarizabilities and the polarizability anisotropies.

Despite of these very encouraging results the finite perturbation SCF CNDO method utilized by Hush and Williams becomes rather laborious when applied to larger molecules. The time-consuming self-consistency process must be repeated for various strengths of the external electric field. Moreover, the procedure of fitting the induced dipole moment to the polynomial in the electric field strength is also open to some objections. It depends on both the polynomial order and the number of points chosen for the interpolation [8]. For these reasons the methods leading directly to the first-order perturbed wave functions and polarizability components seem to be more convenient.

In Part I of this series [9] we studied the application of the variation-perturbation technique of Karplus and Kolker [10, 11] to the calculation of the magnetic susceptibility in the CNDO/2 approximation. It was shown that this semiempirical version of the variation-perturbation procedure leads to nearly the same values of the magnetic susceptibility as those obtained in the non-empirical treatment of Karplus and Kolker. Also the agreement with experimental data was remarkably good. It seems therefore, that the same method should also provide for a reasonable evaluation of the electric polarizability tensor. As will be shown in the next Section, the variation-perturbation technique requires no more than the computation of few simple integrals and can be very easily rewritten within the framework of the CNDO approximation. In comparison with techniques used by Davies and by Hush and Williams it does not involve any iterative procedure and needs only a knowledge of the ground state electronic wave function of a given molecule.

Computational Methods

According to the approximate variation-perturbation scheme developed by Karplus and Kolker [10, 11] the perturbed orbital ψ_i^1 is expressed in the product form

$$\psi_i^1 = f_i \psi_i^0 \quad (1)$$

where ψ_i^0 denotes the unperturbed orbital and the one-electron function f_i is determined by using the variation principle for the second-order energy E^2 . In the Hartree-Fock approximation with neglected self-consistency corrections and with omitted non-local contributions to the Hartree-Fock potential the final formula for E^2 becomes

$$E^2 = 2 \sum_i^n \left[\frac{1}{2} \langle \psi_i^0 | \nabla f_i^* \nabla f_i | \psi_i^0 \rangle + 2 \langle \psi_i^0 | \mathbf{h}' - e_i^1 | f_i \psi_i^0 \rangle - \sum_{j \neq i}^n \{ (e_j^0 - e_i^0) \langle \psi_j^0 | f_i \psi_i^0 \rangle + 2 \langle \psi_j^0 | \mathbf{h}' | \psi_i^0 \rangle \} \langle f_i \psi_i^0 | \psi_j^0 \rangle \right] \quad (2)$$

where \mathbf{h}' represents the one-electron perturbation operator and

$$e_i^1 = \langle \psi_i^0 | \mathbf{h}' | \psi_i^0 \rangle \quad (3)$$

e_k^0 is the energy of the unperturbed orbital ψ_k^0 , the summations in Eq. (2) are performed over all doubly occupied orbitals (n).

In the case of the electric polarizability calculations the perturbation operator for the i -th electron has the following form

$$h'(i) = -\mathcal{E}_\alpha r_\alpha^0(i). \quad (4)$$

\mathcal{E}_α is the α component of the external electric field, and

$$r^0(i) = r(i) - R^0 \quad (5)$$

is the electron coordinate operator referred to the arbitrary chosen origin R^0 . The summation over repeated Greek subscripts is implied.

Writing the function f_i as

$$f_i = -\mathcal{E}_\alpha R_{\alpha i} \quad (6)$$

where $R_{\alpha i}$ are the components of the variational vector function, we obtain the following expression for the electric polarizability tensor

$$\begin{aligned} \alpha_{\mu\nu} = -4 \sum_i^n \left[\frac{1}{2} \langle \psi_i^0 | \nabla R_{\mu i}^* \nabla R_{\nu i} | \psi_i^0 \rangle \right. \\ \left. + 2 \langle \psi_i^0 | r_\mu^0 - \langle r_\mu^0 \rangle_{ii} | R_{\nu i} \psi_i^0 \rangle - \sum_{j \neq i}^n \{ (e_j^0 - e_i^0) \langle \psi_j^0 | R_{\mu i} \psi_i^0 \rangle \right. \\ \left. + 2 \langle \psi_j^0 | r_\mu^0 | \psi_i^0 \rangle \} \langle \psi_i^0 | R_{\nu i}^* | \psi_j^0 \rangle \right] \quad (7) \end{aligned}$$

related to the second order energy (2) by

$$E^2 = -\frac{1}{2} \mathcal{E}_\mu \alpha_{\mu\nu} \mathcal{E}_\nu. \quad (8)$$

In Eq. (7) an abbreviated notation of matrix elements of the electron coordinate

$$\langle r_\mu^0 \rangle_{ii} = \langle \psi_i^0 | r_\mu^0 | \psi_i^0 \rangle \quad (9)$$

has been adopted.

A convenient way for the variational determination of the $R_{\mu i}$ functions is to choose them in a specified analytical form with a number of variational parameters to be determined. Kolker and Karplus [11] have used for $R_{\mu i}$ the polynomial expansions of appropriate symmetry. This procedure results in a set of inhomogeneous linear equations for the determination of variational coefficients. It also follows from the study of Kolker and Karplus [11] that the convergence of the finite polynomial expansion of $R_{\mu i}$ is quite good, especially for the perpendicular component of the polarizability tensor in diatomic molecules. For the parallel component of the polarizability tensor the convergence was not quite as good. Moreover, the calculated parallel components are as a rule much greater than the experimental ones. This indicates that the second order energy obtained by the variation-perturbation treatment of Kolker and Karplus is not an upper bound to the true second-order energy [12, 13]. Apparently, this deficiency of the Kolker and Karplus method is very important in the accurate non-empirical treatment. However, in the case of a simplified semiempirical treatment this shortcoming can partly be reduced.

It is the purpose of this paper to study the applicability of the CNDO/2 version of the variation-perturbation technique to the calculation of the electric polariza-

bility tensor of diatomic molecules. Assuming the convergence of the variation-perturbation scheme we confined our calculations to very simple one- and two-term forms of the polynomial expansion. Taking the origin \mathbf{R}^0 of the coordinate system lying on the internuclear axis (x axis) we have chosen the following form

$$R_{yi} = a_i y^0 + b_i x^0 y^0 \quad (10)$$

for the variational correction in the direction perpendicular to the internuclear axis. The variational correction in the parallel direction was taken in the form

$$R_{xi} = a_i + b_i x^0 \quad (11)$$

with constant a_i determined by the orthogonality condition

$$\langle \psi_i^0 | R_{xi} | \psi_i^0 \rangle = 0.$$

All the coordinates appearing in Eqs. (10) and (11) are measured from the origin \mathbf{R}^0 .

The only integrals which appear after the substitution of Eqs. (10) and (11) into Eq. (7) are of the form

$$\langle \psi_i^0 | (x^0)^k (y^0)^l (z^0)^m | \psi_j^0 \rangle \quad (12)$$

where ψ_i^0 are just the CNDO/2 molecular orbitals or $1s$ Slater atomic orbitals of core electrons¹. Expansion into AO's leads to the following expression

$$\begin{aligned} & \langle \psi_i^0 | (x^0)^k (y^0)^l (z^0)^m | \psi_j^0 \rangle \\ &= \sum_A \sum_B \sum_{\alpha_A} \sum_{\beta_B} c_{i, \alpha_A} C_{j, \beta_B} \langle \alpha_A | (x^0)^k (y^0)^l (z^0)^m | \beta_B \rangle \end{aligned} \quad (12a)$$

where c_{i, α_A} is the LCAO coefficient at atomic orbital α_A of atom A. The integrals over atomic orbitals were further simplified by using the zero differential overlap approximation for all the two-centre distributions, i.e.

$$\langle \alpha_A | (x^0)^k (y^0)^l (z^0)^m | \beta_B \rangle = \langle \alpha_A | (x^0)^k (y^0)^l (z^0)^m | \beta_B \rangle \delta_{AB}. \quad (13)$$

Then, the remaining integrals were calculated with Slater AO's. Moreover, the orthogonality of valence shell orbitals to these describing $1s$ core electrons has been assumed. It seems that the non-orthogonality of $1s$ and $2s$ Slater orbitals should in this case have a little effect on the calculated property.

Obviously, a very short expansion of the variational corrections limits to some extent the scope of the present investigation. In principle, one can use richer polynomial expansions, but then a question arises whether the partial zero differential approximation can be used for higher powers k , l and m in Eq. (13). Its practical utility has only been tested on the first [3, 4] and second [9] moments of the electron distribution.

Finally, it should be pointed out that the molecular orbitals ψ_i^0 used in this paper are those obtained within the original version of the CNDO/2 method. The numerical calculations were programed in Algol for GIER computer and have been performed in the Computational Centre of Warsaw University.

¹ The $1s$ core electrons of atoms other than hydrogen were also taken into account, but the molecular orbitals they occupy were assumed to be equal to the corresponding $1s$ Slater atomic orbitals. The energies ϵ_{1s}^0 were taken from atomic SCF calculations of Clementi [14]. The same procedure has been used previously in the CNDO variation-perturbation treatment of diamagnetic susceptibilities [9].

Results and Discussion

First of all we shall compare our results with those obtained by Kolker and Karplus [11] in the non-empirical variation-perturbation treatment. The corresponding values for the parallel and perpendicular component of the electric polarizability tensor are given in Tables 1 and 2, respectively. In Table 3 a similar comparison is made for the rotational average of the electric polarizability tensor

$$\alpha_{Av} = \frac{1}{2} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}).$$

In these Tables the results of the variation-perturbation treatment by O'Hare and Hurst [15] are also included. In these latter calculations a richer form of the variational correction has been used and also different basis sets were studied. The first column of the O'Hare and Hurst results refer to the BLMO basis set

Table 1. Comparison of the CNDO/2 and non-empirical results of the variation-perturbation calculations for the parallel component of the electric polarizability tensor (all values in 10^{-24} cm^3)

Molecule ^a	This work		Kolker and Karplus [11]		O'Hare and Hurst [15]		
	1-term	2-terms ^b	1-term ^c	2-terms ^c	5-terms ^d		
H*H	1.664	—	1.254	1.293			
H*Li	3.884	4.00	3.25	3.76	3.720 [16]	3.350 [17]	
H*Li*	3.884	—	3.25	3.42			
HF*	0.830	1.168	0.742	0.791	0.907 [16]	1.212 [18]	1.002 [19]
N*N	5.746	4.68	4.58	4.67	4.703 [16]	4.212 [20]	4.043 [21]
F*F	1.904	—	—	—	2.135 [16]	2.245 [22]	
C*O	4.803	—	4.03	4.23	4.651 [16]	3.300 [20]	3.221 [23]
B*F	3.124	—	—	—	4.281 [16]	2.705 [20]	2.716 [23]
LiF*	3.594	—	5.38	11.18			

^a The origin of the coordinate system is taken at the starred nucleus. O'Hare and Hurst [15] used the polynomial expansion centered on both nuclei.

^b Results obtained with the SAMO wave functions of Ransil [16].

^c Results obtained with the BLMO wave functions of Ransil [16].

^d The reference indicates the source of the wave function used in the calculation.

Table 2. Comparison of the CNDO/2 and non-empirical variation-perturbation results for the perpendicular component of the electric polarizability tensor (all values in 10^{-24} cm^3)

Molecule ^a	This work			Kolker and Karplus [11]			O'Hare and Hurst [15]		
	1-term	2-terms	4-terms ^b	1-term ^c	2-terms ^c	4-terms ^c	6-terms ^d		
H*H	0.572	0.572	—	0.716	0.716	0.801			
H*Li	5.571	5.661	6.68	4.05	4.20	5.01			
H*Li*	5.571	5.661	—	4.05	4.20	5.00	5.002 [16]	5.080 [17]	
HF*	0.343	0.377	0.608	0.314	0.331	0.364	0.364 [16]	0.908 [18]	0.791 [19]
N*N	1.098	1.098	1.30	1.18	1.18	1.27	1.251 [16]	1.919 [20]	1.951 [21]
F*F	0.390	0.390	—	—	—	—	0.432 [16]	0.950 [22]	
C*O	1.174	1.283	—	1.35	1.46	1.55	1.562 [16]	2.307 [20]	2.086 [23]
B*F	2.110	2.266	—	—	—	—	2.553 [16]	3.847 [20]	3.738 [23]
LiF*	1.698	4.152	—	3.40	6.24	10.53			

For Footnotes see Table 1.

Table 3. Comparison of the CNDO/2 and non-empirical variation-perturbation results for the rotational average of the electric polarizability tensor (all values in 10^{-24} cm^3)

Molecule ^a	This work		Kolker and Karplus [11]		O'Hare and Hurst [15]		
	2/1-terms ^b	4/2-terms ^{b,c}	2/1-terms ^{b,d}	4/2-terms ^{b,d}	6/5-terms ^e		
H*H	0.936	—	0.890	0.965			
H*Li	5.069	5.79	3.88	4.59	4.575 [16]	4.503 [17]	
HF*	0.528	0.795	0.468	0.506	0.546 [16]	1.009 [18]	0.861 [19]
N*N	2.648	2.43	2.28	2.40	2.403 [16]	2.684 [20]	2.651 [21]
F*F	0.895	—	—	—	1.000 [16]	1.382 [22]	
C*O	2.283	—	2.32	2.44	2.592 [16]	2.639 [20]	2.466 [23]
B*F	2.552	—	—	—	3.128 [16]	3.476 [20]	3.398 [23]
LiF*	3.966	—	5.95	10.75			

^a See Footnote a of Table 1.

^b The symbol n/m indicates the number of terms in $R_{\mu i}$ for the perpendicular (n) and parallel (m) direction.

^c See Footnote b of Table 1.

^d See Footnote c of Table 1.

^e See Footnote d of Table 1.

of Ransil [16]. The same basis set has also been employed by Kolker and Karplus. The other columns of the O'Hare and Hurst results correspond to the calculations with extended basis sets.

As one can see, there is a quite remarkable agreement between the present CNDO/2 results and those obtained in non-empirical calculations of Kolker and Karplus. Except for LiF the simplified CNDO variation-perturbation treatment leads to reasonable values of both components as well as the rotational average of the electric polarizability tensor. For LiF the non-empirical result appears to be anomalously high and also Kolker and Karplus considered this molecule as an exception.

Some larger differences are observed for the parallel component of the electric polarizability of H_2 and N_2 . In the case of the hydrogen molecule this too large value of α_{\parallel} can partly be ascribed to the use of the zero differential approximation. It should be pointed out, that in the series of molecules studied in this paper, the overlap integral for $1s$ orbitals in the hydrogen molecule has the largest numerical value. The source of the too large value of α_{\parallel} for N_2 molecule seems, however, to be different. Perhaps, the Slater orbitals utilized in the CNDO/2 calculations are partly responsible for the observed discrepancy.

It also follows from Tables 1 and 2, that the difference between the CNDO/2 and non-empirical results becomes more pronounced when better molecular wave functions are used. Nevertheless, the rotational average α_{Av} calculated by using the CNDO/2 version of the variation-perturbation approach is still in reasonable agreement with non-empirical results. Thus, the present method seems to be quite useful for a simple evaluation of α_{Av} . It is also worth noting, that the CNDO/2 version of the variation-perturbation method does not require approximations other than already involved in the CNDO/2 HFR SCF procedure [3, 4].

The results of various CNDO/2 calculations of α_{Av} and the experimental data are compared in Table 4. Unfortunately, the experimental data are too scarce to

Table 4. Rotational average of the polarizability tensor – a comparison of various CNDO/2 results (all values in 10^{-24} cm^3)

Molecule	CNDO/2 results					Obs. [24]
	This work	Davies [5]		Hush and Williams		
		I ^a	II ^b	I ^c [6]	II ^d [7]	
HH	0.936	0.07	1.33	0.152	0.820	0.819
HLi	5.069	—	—	—	—	—
HB	2.873	—	—	—	—	—
HF	0.528	0.13	0.36	—	1.019	—
NN	2.648	0.63	—	0.647	1.800	1.767
FF	0.895	—	—	0.323	1.476	—
CO	2.283	—	—	0.829	1.982	1.977
BF	2.552	—	—	1.987	3.140	—
LiF	3.966	—	—	0.833	1.986	—

^a Perturbed Hartree-Fock calculations without $2p$ hydrogen orbitals.

^b Perturbed Hartree-Fock calculations with $2p$ orbitals at hydrogen.

^c Results of the finite electric field perturbation method without empirical corrections.

^d Results of the finite electric field perturbation method with empirical corrections for atomic contributions.

Table 5. Polarizability anisotropies $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ (all values in 10^{-24} cm^3)

Molecule	CNDO/2 results				Obs. [24]	Non-empirical calculations		
	This work	Davies [5]	Hurst and Williams [6]					
		I ^a	II ^b					
HH	1.092	0.21	0.40	0.455	0.314	0.2671 [25]		
HLi	-1.777	—	—	—	—	-1.282 [15], -1.730 [15]		
HB	-0.159	—	—	—	—			
HF	0.453	0.29	0.41	0.327	—	0.236 [26], 0.210 [15]	0.543 [15],	0.305 [15],
NN	4.648	0.70	—	0.759	0.696	3.451 [15],	2.291 [15],	2.092 [15]
FF	1.904	—	—	0.919	—	1.37 [27],	1.703 [15],	1.298 [15]
CO	3.520	—	—	0.361	0.532	3.090 [15],	0.993 [15],	1.135 [15]
BF	0.858	—	—	-1.317	—	1.729 [15],	-1.142 [15],	-1.024 [15]
LiF	-0.558	—	—	0.500	—			

^a See Footnote a of Table 4.

^b See Footnote b of Table 4.

allow for a sophisticated judgement. Nevertheless, the present method seems to be essentially better than that proposed by Davies [5]. Our results seem also to be better than those obtained by Hush and Williams [6] in the finite perturbation approach without empirical corrections. However, the finite perturbation method extended by an empirical correction scheme [7] gives results which are much closer to the existing experimental data than the present ones.

The calculated and observed polarizability anisotropies are shown in Table 5. Both, the method of Hush and Williams [6, 7] and the method of Davies [5] lead to better results than the CNDO/2 variation-perturbation approach. It seems, that sufficiently accurate computation of the polarizability anisotropies lies beyond

the abilities of the CNDO/2 variation-perturbation approach in its present form. The same, however, applies also to the non-empirical calculations, especially to those based on the approximate variation-perturbation technique of Karplus and Kolker.

According to results obtained in the present paper, the CNDO/2 version of the variation-perturbation approach can serve as a simple and useful tool for the calculation of rotational averages of the electric polarizability tensor. In comparison with other semiempirical methods discussed in this paper, our CNDO/2 variation-perturbation approach is much simpler from the computational point of view. It requires only a knowledge of the ground state wave function and the calculation of few simple integrals. Unfortunately, this attractive approach cannot allow for a reasonable evaluation of the polarizability anisotropies. This conclusion is quite opposite to that drawn out in connection with the CNDO/2 variation-perturbation calculations of the magnetic susceptibility tensor [9]. In this latter case, the rotational average as well as the individual components were predicted in good agreement with experimental data and non-empirical results. It should be pointed out, that the observed difference between the electric polarizability and magnetic susceptibility calculations within the CNDO/2 variation-perturbation approach resembles that found by Kolker and Karplus [11] in the case of the non-empirical treatment. Thus, the lack of a good agreement between the calculated and observed polarizability components can also be ascribed to the use of the variation-perturbation technique [28].

Finally, it is worth noting, that our results are frequently in remarkably good agreement with non-empirical variation-perturbation calculations which employ the minimal Slater orbital basis set. Hence, it follows that the CNDO/2 variation-perturbation method is able to simulate these non-empirical results. This observation also partly justifies the use of the zero differential overlap approximation which works unexpectedly good.

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