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The Calculations of Dipole Polarizabilities and Anisotropies by the CNDO Method: The Effect of an Extended-basis Set

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The dipole polarizabilities and the anisotropies of several small molecules have been calculated according to a formula derived from the time-dependent perturbation theory. The wave functions and the energies were calculated by means of the CNDO-CI version, with an extended-basis set. The effects on the calculated results of the introduction of the atomic vacant orbitals into the basis set have been discussed.

Theoretical calculations of polarizabilities within the framework of the CNDO version have been performed by several investigators.1–4) Miyazaki and one of the present authors1) reported their theoretical calculations of polarizabilities according to the formula derived from the time-dependent perturbation theory. They calculated the polarizabilities by the use of the wave functions and the energies, which were evaluated by the CNDO-CI method using the valence-orbital-basis set. They discussed the effects of the parameters in the CNDO method on the calculated polarizabilities and concluded that the calculated polarizabilities were generally smaller than the experimental results and that the calculated anisotropies were larger than the observed results. Hush and Williams2) used the finite perturbation theory with the valence-orbital-basis set in order to investigate the polarizabilities and the anisotropies of axial symmetric molecules. Their calculated values of polarizability-anisotropy, $\alpha_{\parallel}$-$\alpha_{\perp}$, were in good agreement with the experimental ones. However, the calculated values of the polarizabilities were small in comparison with the experimental ones, and the calculated vaules of the anisotropies were larger than the observed ones. They improved the calculated results by adding the correction terms to the diagonal elements of the molecular polarizability tensors.3) Davies4) calculated the polarizabilities of several small molecules by the use of the self-consistent perturbation method. From a comparison between the results of calculations in which the 2p-orbitals of the hydrogen atoms are considered and those in which they are not, he concluded that the valence-orbital-basis set is inadequate for the representation of the perturbed wave functions. At any rate, the polarizabilities calculated within the framework of the CNDO version with the valence-orbital-basis set were not in agreement with the experimental ones.

The purpose of this work is to investigate the effect on the calculated polarizabilities of the introduction of the atomic vacant orbitals into the basis set. The RCNDO method proposed by Salahub and Sandorfy5) is a modified CNDO method with the extended-basis set. This method is, however, not always appropriate for the calculation of the polarizability, as will be shown later. Then the trial method, which differs from the RCNDO method, has been used to obtain the wave functions and the energies. Discussions have been based on a comparison of the results calculated by several approaches.

Methods of Calculations

Polarizability and Anisotropy: The polarizability, α, of a system in the electromagnetic field as a perturbation can be derived from the time-dependent perturbation theory.1) By averaging the vector quantities over all the orientations of the system with respect to the field, α can be given as:

$$\alpha = \frac{2}{3h}\sum_{b}\frac{\nu_{ba}|\langle\Psi_a^\circ|e\sum_i \boldsymbol{r}_i|\Psi_b^\circ\rangle|^2}{\nu_{ba}^2-\nu^2}, \qquad (1)$$

where $\boldsymbol{r}_i$ is the position vector of the i-th electron; ν is the frequency of the incident light, and $h\nu_{ba}=E_b-E_a$; here E_a is the energy of the unperturbed ground state described by the wave function, Ψ_a°, and E_b is the energy of the unperturbed excited state with the wave function of Ψ_b°. The anisotropy, k, is expressed by the components of the polarizability tensor as follows:

$$k^2 = \{(\alpha-\alpha_1)^2+(\alpha-\alpha_2)^2+(\alpha-\alpha_3)^2\}/6\alpha^2, \qquad (2)$$

where α_1, α_2, and α_3 are the principal polarizabilities of the system.

Molecular Orbital Calculations: The molecular wave function, Ψ_a°, of an unperturbed ground state is described as the single Slater-determinant with a closed-shell structure, while those of unperturbed excited states, Ψ_b°'s, are described as linear combinations of all the singly-excited configurations obtained by the configuration-interaction (CI) treatment.

The atomic vacant orbitals considered in this work, in addition to the valence orbitals, have been restricted to those with a principal quantum number (p.q.n.) greater by 1 than that of the valence orbitals, and the effective nuclear charges for the atomic vacant orbitals are taken to be equal to those for the valence orbitals as determined by Slater's rule. Within the framework of the CNDO version, the diagonal element of the SCF energy matrix in the Roothaan LCAO-SCF equation6) can be written as follows:7)

$$F_{\mu\mu} = -I_\mu - (Z_{\rm A}-1)\gamma_{\rm AA}^{n\bar{m}} - \sum_{{\rm B}\neq{\rm A}} Z_{\rm B}\gamma_{\rm AB}^{n\bar{m}} + \left(P_{\rm AA}^{nn}-\frac{1}{2}P_{\mu\mu}\right)\gamma_{\rm AA}^{nn} + \sum_{m\neq n}^{\rm A} P_{\rm AA}^{mm}\gamma_{\rm AA}^{nm} + \sum_{{\rm B}\neq{\rm A}}\sum_{m}^{\rm B} P_{\rm BB}^{mm}\gamma_{\rm AB}^{nm}, \qquad (3)$$

where n is the p.q.n. of the atomic orbital, φ_μ, which belongs to the A atom; I_μ, the average ionization potential of φ_μ; $Z_{\rm A}$ and $Z_{\rm B}$, the core charges of the A and B atoms respectively; $P_{\mu\mu}$, the charge density of φ_μ; and $P_{\rm AA}^{mm}$, the sum of the charge densities of

TABLE 1. AVERAGE IONIZATION POTENTIALS, I_μ, FOR ATOMIC VACANT ORBITALS (eV)

Atom	Orbital	I_μ
H	2s	3.399
	2p	3.399
C	3s	3.735
	3p	2.509
	3d	1.551
N	3s	4.329
	3p	3.144
	3d	2.456
O	3s	4.378
	3p	3.053
	3d	2.657

the atomic orbitals with the p.q.n. -m on the A atom; $\gamma_{AB}^{n\bar{m}}$ represents the repulsion between electrons in φ_μ and in the atomic orbital with the p.q.n. -m on the B atom, and $\bar{m}$ in $\gamma_{AB}^{n\bar{m}}$ is the p.q.n. of the valence orbital on the B atom. The electronic repulsion integral, γ_{AB}^{nm}, is calculated as a Coulomb integral including the ns and ms Slater orbitals. The values of the average ionization potentials for valence orbitals followed those of the CNDO/1 method,[7)] while those of the vacant orbitals were evaluated from the table in Ref. 8 and are shown in Table 1. The off-diagonal element of the SCF energy matrix is described as follows:

$$F_{\mu\nu} = \beta_{AB}^{nm} S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB}^{nm}, \tag{4}$$

where n is the p.q.n. of φ_μ on the A atom; m, the p.q.n. of φ_ν on the B atom; $S_{\mu\nu}$, the overlap integral between φ_μ and φ_ν, and $P_{\mu\nu}$, the bond order between φ_μ and φ_ν. The bonding parameter, β_{AB}^{nm}, is approximated by:

$$\beta_{AB}^{nm} = \frac{1}{2} \kappa (\beta_A^\circ + \beta_B^\circ), \tag{5}$$

where the values of the β_A° and β_B° are the same as those used in the CNDO/1 method[7)] and where the κ parameter is determined as will be described below. The value of κ for the interaction between valence orbitals is taken to be unity, as in the CNDO/1 method. The average ionization potentials of the 2p-orbitals for the first-row elements are nearly equal to a half of the values of the β_A° and are roughly five times the average ionization potentials of 3p-orbitals. Therefore, the value of κ for the interaction between vacant orbitals is taken to be 0.2. The value of κ for the valence orbital-vacant orbital interaction is taken to be 0.6, the mean of 1.0 and 0.2. The geometries of the molecules followed the data listed in Ref. 9.

Results and Discussion

By the use of the molecular wave functions obtained from the CNDO/2-CI treatment including all the singly- and the doubly-excited configurations, Tatematsu[10)] calculated the polarizabilities of several molecules according to the formula shown in Eq. (1). The calculated values were 0.504, 0.685, 0.721, and 1.128 Å^3 for N_2, CO, C_2H_2, and C_2H_4 respectively. These values are smaller than those obtained by the calculations considering only the singly-excited configurations in Ref. 1. However, the calculated anisotropies were slightly improved by considering the doubly-excited configurations, although they, as well as those in Ref. 1, are larger than the experimental ones. The electronic transition energies and the transition moments calculated by the CNDO/2-CI method are listed in Table 2 for N_2 as an example. The introduction of doubly-excited configurations reduces the transition moments in the calculation with only the singly-excited configurations and brings about new excited states which have large electronic excitation energies and small transition moments, so that the new ones contribute scarcely anything to the polarizability. The above discussions showed that the CI treatment including the doubly-excited configurations does not bring a drastic improvement in the calculation of polarizabilities, although the treatment is a powerful approach to an investigation of several lower electronic excited states.[11)] In this study, therefore, calculations have been performed with the CI treatment including only the singly-excited configurations.

The polarizability and the anisotropy of C_2H_2 were calculated with various basis sets; the results are shown in Table 3. With the increase in the number of atomic orbitals in the basis set, the value of the polarizability increases and the value of the anisotropy decreases. In the investigation by Davies,[4)] the 2p-orbitals of the hydrogen atom were used in the basis set for the perturbed wave functions, but the 2s-orbital was not considered. From the comparisons between the results of (D) and (F) and between those of (E) and (G) shown in Table 3, it is found that the introduction of the 2s-orbital of the hydrogen atom, in addition to the 2p-orbitals, into the basis set effectively improves the calculated results. The results in (F), (G), and (H) lead to the following discussion of the effects of the vacant orbitals of the carbon atom on the calculated results for the polarizability and the anisotropy. The value of the polarizability calculated by considering the 3s-, 3p-, and 3d-orbitals of the carbon atom, (H) in the table, is larger than the experimental one. On the other hand, the values of the polarizability in (F) and (G) are slightly smaller than the observed one. From a comparison between the results in (F) and (G), it is found that (F), including the 3s- and 3p-orbitals of the carbon arom, yields the good polarizability, while (G), including the 3d-orbitals, yields a good anisotropy.

On the basis of the above discussion of the results of C_2H_2, it is decided that two kinds of basis sets will be used in the following calculations. One of them contains the 1s-, 2s-, and 2p-orbitals of a hydrogen atom and the 2s-, 2p-, 3s-, and 3p-orbitals of first-row elements. The other one contains the 1s-, 2s-, and 2p-orbitals of a hydrogen atom and the 2s-, 2p-, and 3d-orbitals of first-row elements. The molecular orbital calculation with the former basis set will be

TABLE 2. THE ELECTRONIC TRANSITION ENERGIES AND THE TRANSITION MOMENTS OF N_2 CALCULATED BY THE CNDO-CI METHOD.[a]

SCI[b]				DCI[b,c]			
Transition energy [eV]	Transition moment[D]			Transition energy[eV]	Transition moment[D]		
	M_x	M_y	M_z		M_x	M_y	M_z
15.253	2.2051	0	0	15.861	2.1495	0	0
15.253	0	2.2051	0	15.861	0	2.1495	0
15.598	0	0	−1.5896	17.479	0	0	−0.9867
24.257	0	0	4.6430	26.153	0	0	3.6547
				26.615	−0.1773	0	0
				26.615	0	−0.1773	0
				32.696	−0.3635	0	0
				32.696	0	−0.3635	0
				37.359	0.0356	0	0
				37.359	0	0.0356	0
				41.842	−0.0495	0	0
				41.842	0	−0.0495	0
				43.450	0.0871	0	0
				43.450	0.0	0.0871	0
				44.323	0	0	−0.2429
50.530	0	0	−2.5074	50.936	0	0	−1.2594
				51.633	−0.0339	0	0
				51.633	0	−0.0339	0

a) The z-axis is the bond axis of N_2. b) SCI means the calculation including only the singly-excited configurations while DCI does the CI calculation including all the singly- and doubly-excited configurations. c) The excited states which have the transition energies larger than 51.633 eV are omitted from the table because of their negligible contributions to the polarizability.

TABLE 3. THE POLARIZABILITIES AND THE ANISOTROPIES OF C_2H_2 CALCULATED WITH VARIOUS BASIS SET

	N[a]	Atomic orbitals in a basis set		Polarizability (Å)	Anisotropy
		Hydrogen	Carbon		
(A)	10	1s	2s, 2p	1.052	0.671
(B)	16	1s, 2p	2s, 2p	2.006	0.701
(C)	18	1s, 2s, 2p	2s, 2p	2.549	0.462
(D)	24	1s, 2p	2s, 2p, 3s, 3p	3.039	0.428
(E)	26	1s, 2p	2s, 2p, 3d	2.950	0.363
(F)	26	1s, 2s, 2p	2s, 2p, 3s, 3p	3.438	0.343
(G)	28	1s, 2s, 2p	2s, 2p, 3d	3.292	0.280
(H)	36	1s, 2s, 2p	2s, 2p, 3s, 3p, 3d	5.968	0.136
obsd[b]				3.49	0.178

a) N is the number of atomic orbitals in the basis set. b) From Ref. 12.

TABLE 4. POLARIZABILITIES CALCULATED BY SEVERAL MO METHODS (Å^3)

	EB/sp[a]	EB/d[a]	EB/sp′ [a]	RCNDO[a]	RCNDO/v[a]	CNDO/2[a]	obsd[b]
N_2	1.807	1,832	1.959	1.409	1.289	0.754	1.77
CO	2.087	2 092	2.264	1·657	1.507	0.933	1.97
CO_2	2.815	2.336	3.178	2.522	2.375	1.189	2.63
C_2H_2	3.438	3.292	4.340	2.369	1.754	1.028	3.49
C_2H_4	4.492	4.660	5.363	3.386	2.303	1.497	4.22
C_2H_6	5.402	5.840	5.965	3.290	1.859	1.376	4.47
CH_4	3.078	3.289	3.449	1.843	0.877	0.644	2.60[c]
NH_3	2.387	2.566	2.961	1.456	0.810	0.547	2.22

a) See text. b) From Ref. 12. c) From Ref. 13,

TABLE 5. ANISOTROPIES CALCULATED BY SEVERAL MO METHODS

	EB/sp[a]	EB/d[a]	EB/sp′ [a]	RCNDO[a]	RCNDO/v[a]	CNDO/2[a]	obsd[b]
N_2	0.232	0.132	0.016	0.522	0.575	0.472	0.131
CO	0.229	0.082	0.052	0.329	0.362	0.236	0.090
CO_2	0.426	0.517	0.379	0.703	0.751	0.717	0.266
C_2H_2	0.343	0.280	0.135	0.528	0.715	0.683	0.178
C_2H_4	0.250	0.228	0.058	0.316	0.466	0.446	0.143
C_2H_6	0.124	0.185	0.016	0.001	0.023	0.019	0.058
CH_4	0	0	0	0	0	0	0[c]
NH_3	0.061	0.063	0.030	0.183	0.333	0.286	0.043

a) See text. b) From Ref. 12. c) From Ref. 13.

called EB/sp (Extended-basis Set containing 3s- and 3p-orbitals) method for short and the latter, the EB/d (Extended-basis Set containing 3d-orbitals) method. The calculated polarizabilities are listed in Table 4. In the table the values calculated by the use of the wave functions obtained from other molecular orbital calculations are also shown. The results calculated using the EB/sp and the EB/d methods are improved as compared with those from the CNDO method used in the previous work.[1] Also, the results from the RCNDO/v method are improved by the use of the RCNDO method; here, RCNDO/v means the RCNDO calculation without the vacant orbitals. However, the RCNDO method gives poor results for the polarizabilities in comparison with those of the EB/sp and the EB/d methods. There are differences between the orbital exponents of the vacant orbitals used in the RCNDO method and the method in this work and between the estimations of the molecular integrals in these methods. It is considered that the introduction of the different orbital exponents is not the direct cause of the inferiority of the RCNDO method, because the results from the EB/sp′ method, which is the EB/sp calculation with the same orbital exponents as those in the RCNDO method except for a hydrogen atom, are rather analogous to those calculated by the EB/sp method.

The calculated anisotropies are listed in Table 5. Most of the calculated results are larger than the experimental ones. The values calculated by the CNDO/2 method are much improved by the EB/sp and the EB/d methods. For the calculation of the anisotropies as well as the polarizabilities, the RCNDO method is inferior to both the EB/sp and the EB/d methods. The inferiority of the RCNDO method may be caused by the estimation of the bonding parameter for the valence orbital-vacant orbital interaction. In the RCNDO method, the bonding parameter, β^{nm}_{AB}, was given by the following expression:

$$\beta^{nm}_{AB} = \eta(I^n_A + I^m_B),$$

where I^n_A is the average of the ns- and the np-ionization potentials of the A atom and where η was taken

TABLE 6. THE WEIGHTS OF THE VACANT ORBITALS IN THE GROUND STATE WAVE FUNCTIONS (%)

Molecule	EB/sp[a]	EB/d[a]	EB/sp′ [a]	RCNDO[a]
CO	9.04	6.90	4.44	0.02
CO_2	7.71	13.1	3.91	0.02
CH_4	18.8	15.4	16.2	0.375

a) See text.

TABLE 7. COMPARISON OF THE PRESENT RESULTS OF THE POLARIZABILITIES WITH THOSE IN THE NON-EMPIRICAL CALCULATIONS[a]

			CO	CH_4
UPHF[b]				
Ref. 13	one term			2.819
	three terms		2.384	3.171
	four terms		2.429	3.179
EB/sp			2.087	3.078
EB/d			2.092	3.289
obsd			1.97	2.60

CPHF[c]			
CH_4			
	N[d]	α	Basis Set
Ref. 15	22	1.073	$1s_C$, $1s'_C$, $2s_C$, $2s'_C$, $3s_C$, $2p_C$, $2p'_C$, $2p''_C$, $1s_H$, $2s_H$
	27	1.751	$1s_C$, $1s'_C$, $2s_C$, $2s'_C$, $3s_C$, $2p_C$, $2p'_C$, $2p''_C$, $3d_C$, $1s_H$, $2s_H$
	39	1.398	$1s_C$, $1s'_C$, $2s_C$, $2s'_C$, $3s_C$, $2p_C$, $2p'_C$, $2p''_C$, $1s_H$, $2s_H$, $2p_H$
	39	1.831	$1s_C$, $1s'_C$, $2s_C$, $2s'_C$, $3s_C$, $2p_C$, $2p'_C$, $2p''_C$, $3d_C$, $1s_H$, $2s_H$, $2p_H$
EB/sp	28	3.078	$2s_C$, $2p_C$, $3s_C$, $3p_C$, $1s_H$, $2s_H$, $2p_H$
EB/d	29	3.289	$2s_C$, $2p_C$, $3d_C$, $1s_H$, $2s_H$, $2p_H$
obsd		2.60	
NH_3			
Ref. 16	8	0.624	$1s_N$, $2s_N$, $2p_N$, $1s_H$
	16	0.930	$1s_N$, $1s'_N$, $2s_N$, $2s'_N$, $2p_N$, $2p'_N$, $1s_H$, $1s'_H$
	31	1.386	$1s_N$, $1s'_N$, $2s_N$, $2s'_N$, $2s''_N$, $2p_N$, $2p'_N$, $3d_N$, $1s_H$, $1s'_H$, $2p_H$, $1s_{CLP}$[e]
EB/sp	23	2.387	$2s_N$, $2p_N$, $3s_N$, $3p_N$, $1s_H$, $2s_H$, $2p_H$
EB/d	24	2.566	$2s_N$, $2p_N$, $3d_N$, $1s_H$, $2s_H$, $2p_H$
obsd		2.22	

a) Units in Å³. b) The uncoupled perturbed Hartree Fock method. c) The coupled perturbed Hartree Fock method. d) The number of the atomic orbitals. e) Located upon the estimated centroid of the lone pair (0.7 a.u. from N).

as 0.4 for the valence orbital-valence orbital interaction and as 0.05 for all the others. By comparing the equation with Eq. (5), it is found that the values of the β_{AB}^{nm} for the valence orbital-vacant orbital interaction in the RCNDO method are smaller than those given by Eq. (5). The influence of the bonding parameters appears in the weights of the atomic vacant orbitals in the wave functions of the ground state. Some of the calculated results for the weights are shown in Table 6. The weights in the RCNDO method are very small in comparison with those in the other methods. The results obtained by the RCNDO method may be improved by the introduction of some other vacant orbitals, for example, 3d-orbitals of first-row elements, into the basis set, because the calculated values of the polarizabilities increase with the number of atomic orbitals, as has been shown in Table 3.

Finally, some results of the polarizabilities in the present work will be compared with those in the non-empirical calculations. The results are listed in Table 7. The values calculated by Liebmann and Moskowitz[13)] by means of the uncoupled perturbed Hartree Fock (UPHF) method with the variation technique are larger than the experimental ones; this is the case even when the polynomial in the perturbing variable is restricted to only one term. The overestimation is not due to the zeroth-order wave function used in the calculation, because it appeared also in the results of the UPHF method using the other zeroth-order wave functions.[14)] Arrighini *et al.*[15,16)] used several basis sets for each molecule in the coupled perturbed Hartree Fock (CPHF) calculation in order to discuss the effect of the basis sets and concluded that their choice of the basis sets was improper for the polarizabilities because even their largest basis set yielded a small polarizability. The results obtained by the EB/sp and the EB/d methods seem to be good in comparison with those obtained by the non-empirical ones. Because of the results for C_2H_2 in Table 3, however, it can not be said that the basis sets used in the present work bring a convergence of the polarizabilities. The present work is not appropriate as the basis of a discussion of the convergence, which is rather an interesting subject for a non-empirical calculation.

From a consideration of the results in Tables 3—6, it may be said that the effect of the atomic vacant orbitals on the calculated polarizabilities is not independent of the parameter values in the molecular integrals and that good results for the polarizabilities can be obtained by the calculation with the basis set in the EB/sp or the EB/d methods if the parameter values are suitably determined. The influences of the introduction of the atomic vacant orbitals and of the parameter values on some other physical values will be investigated in future studies.

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