Theoret. chim. Acta (Berl.) 11, 254—262 (1968)

Semi-Empirical All Valence Electrons SCF-MO-CNDO Theory

IV. Dipole Moments

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Received February 6, May 28, 1968

The calculation of molecular dipole moments in the SCF-MO-CNDO theory is considered. The question of translational invariance is examined, and it is shown that the formula for dipole moments used in MO theories including overlap cannot be used in the CNDO approximation. The Pople-Segal formula for dipole moments is shown to be the most accurate of several approximate formulae with the required invariance property.

For molecules containing only hydrogen and first-row atoms, the semi-empirical SCF-MO-CNDO theory predicts dipole moments about as accurately as the Pople-Segal CNDO/2 theory, and much more accurately than the Extended Hückel Theory. For molecules containing heavier atoms, the semi-empirical theory fails.

Die Schwierigkeiten einer Berechnung von Dipolmomenten im Rahmen der SCF-MO-CNDO-Methode und die Frage nach der Translationsinvarianz werden diskutiert. Die besten Ergebnisse liefert die Pople-Segal-Formel. Dipolmomente von Molekülen, die nur aus Wasserstoff und Elementen der ersten Periode bestehen, werden mit unserer semiempirischen SCF-MO-CNDO-Methode wie mit der Pople-Segalschen CNDO/2-Methode ähnlich gut und beträchtlich genauer als mit der erweiterten Hückel-Methode erhalten. Bei Molekülen mit schwereren Atomen sind die Ergebnisse unbefriedigend.

On traite les moments dipolaires moléculaires dans la théorie SCF-MO-CNDO. On a montré que la formule pour le moment dipolaire utilisé dans la théorie MO en tenant compte de recouvrement ne peut pas être utilisée dans l'approximation CNDO. Entre les différentes formules approximative la formula de Pople-Segal pour les moments dipolaires est montrée d'être la meilleure. Pour les molécules qui ne consistent que d'hydrogène et des atomes de premier rang la théorie semiempirique SCF-MO-CNDO donne des moments dipolaires presque aussi exact que la théorie de Pople-Segal CNDO/2 et beaucoup plus exact que la théorie d'Hückel extensé. Pour les molécules contenants des atomes plus graves la théorie manque.

A. Introduction

In Parts II [1 a] and III [1 b] of this series [1 a, 1 b, 2] it was shown that the use of atomic parameters derived from valence state energies [2] and empirical bonding parameters [1 a] in SCF-MO-CNDO calculations [3, 4, 5] resulted in more accurate bonding energies [1 b] and orbital energies [1 a] than those obtained using theoretically-based parameters in SCF-MO-CNDO calculations. In the final two papers, the effect of using semi-empirical atomic and bonding parameters on the charge distribution is considered.

In this paper the values of the dipole moments calculated from the SCF-MO-CNDO theory, using both semi-empirical and theoretical parameters, and those calculated using the Extended Hückel Theory [6] are compared with experimental results.

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B. Calculation of Dipole Moments

In a closed-shell molecule, each molecular orbital is doubly occupied, so that the dipole moment in the x-direction is

$$\mu_x = -2e \sum_i \int \psi_i^* x \psi_i \, dV + e \sum_A Z_A X_A . \tag{1}$$

Since the M.O. calculations include valence electrons only, Z_A is the charge of the core of atom A, including both the nucleus and inner shell electrons.

In matrix form, Eq. (1) becomes

$$\mu_x = -e \operatorname{tr} \boldsymbol{PX} + e \sum_A Z_A X_A \tag{2}$$

where $\boldsymbol{P}$ is the population matrix and the matrix elements of $\boldsymbol{X}$ are the dipole integrals $X_{kl} = \int \phi_k^* X \phi_l \, dV$.

Equation (2) is used to compute dipole moments for the wave functions calculated using the Extended Hückel Theory. For the SCF-MO theory with the CNDO approximation, however, Eq. (2) must be modified in order to preserve invariance with respect to translation of axes, as the dipole moment of a neutral molecule is invariant with respect to translation.

Consider the transformation of co-ordinates

$$x' = x - x_0 , \quad y' = y, \quad z' = z . \tag{3}$$

Under this transformation, Eq. (2) for the dipole moment is transformed to

$$\mu'_x = -e \operatorname{tr} \boldsymbol{PX}' + e \sum_A Z_A X'_A \tag{4}$$

in which the transformed dipole integrals, X'_{kl}, are given by

$$X'_{kl} = \int \phi_k^* (x - x_0) \phi_l \, dV = X_{kl} - x_0 S_{kl} . \tag{5}$$

The nuclear co-ordinates transform according to Eq. (3), so that

$$\mu'_x = -e \operatorname{tr} \boldsymbol{P}(\boldsymbol{X} - x_0 \boldsymbol{S}) + e \sum_A Z_A (X_A - x_0) . \tag{6}$$

From Eq. (2) and (6), the transformation rule for the dipole moment is

$$\mu'_x = \mu_x + e x_0 \left(\operatorname{tr} \boldsymbol{PS} - \sum_A Z_A \right) . \tag{7}$$

For molecular orbital theories in which overlap is included, the orthonormality condition for the orbitals is

$$\sum_k \sum_l C_{ki}^* C_{li} S_{kl} = \delta_{ij} \tag{8}$$

so that the total number of (valence-shell) electrons in a closed-shell molecule is

$$N = 2 \sum_i \sum_k \sum_l C_{ki}^* C_{li} S_{kl} = \sum_k \sum_l P_{kl} = \operatorname{tr} \boldsymbol{PS} \tag{9}$$

and the dipole moment is invariant for a neutral molecule.

If overlap is neglected, the dipole moment transforms as

$$\mu'_x = \mu_x + e x_0 \operatorname{tr} \boldsymbol{P}(\boldsymbol{S} - \boldsymbol{I}) . \tag{10}$$

Equation (2) cannot be used, therefore, to compute the dipole moment when the molecular orbitals have been calculated without overlap.

There are several ways to calculate an approximate dipole moment, which is invariant under translation of axes, for the SCF-MO-CNDO theory.

(i) The dipole moment can be calculated by assuming that the electron population of each atom is a point charge at the nucleus, so that

$$\mu_x = e \sum_{\mathrm{A}} (Z_{\mathrm{A}} - P_{\mathrm{AA}}) X_{\mathrm{A}} . \tag{11}$$

Equation (11) is clearly invariant with respect to translation for a neutral molecule, and is in one sense consistent with the CNDO approximation, since with this approximation, the dipole integrals between different atomic orbitals vanish, and the dipole moment is

$$\mu_x = -e \sum_{k} P_{kk} X_{kk} + e \sum_{\mathrm{A}} Z_{\mathrm{A}} X_{\mathrm{A}} . \tag{12}$$

The centre of charge of a pure s or p orbital is at the nucleus, so that for an $s-p$ basis set, Eq. (12) is identical with Eq. (11). However, this is not true for a hybrid basis set since the centre of charge of a hybrid orbital is not at the nucleus. In molecules with lone pairs, the displacement of the centre of the electron population of an atom away from the nucleus makes a substantial contribution to the molecular dipole moment [4, 7, 8, 9]. This atomic polarization effect is not included in the point-charge approximation.

(ii) Pople and Segal [4] neglected all the diatomic dipole integrals in Eq. (2), but included the dipole integrals for different orbitals on the same atom, so that the dipole moment is given by

$$\mu'_x = -e \sum_{k} \sum_{l} P_{kl} X_{kl} \theta_{kl} + e \sum_{\mathrm{A}} Z_{\mathrm{A}} X_{\mathrm{A}} \tag{13}$$

where:

$$\theta_{kl} = \begin{cases} 1 & \text{if } \phi_k \text{ and } \phi_l \text{ are on the same atom,} \\ 0 & \text{otherwise,} \end{cases}$$

as in the NDDO approximation [3].

Equation (13) is invariant to translation, since atomic orbitals of the same atom are orthogonal, and it is also invariant to rotation and hybridization, since the dipole integrals X_{kl} of a given atom transform in the required way [3].

For a basis of pure s and p orbitals, the only non-zero dipole integral for different orbitals on the same atom are X_{s,p_x}, Y_{s,p_y}, Z_{s,p_z}. The terms containing these integrals represent the atomic polarization effect, which is omitted in the point-charge formula, Eq. (11). For Slater orbitals [44], X_{s,p_x} is found by elementary integration to be

$$X_{s,p_x} = \int \phi_s \, x \, \phi_{p_x} \, dV = \frac{n'(n' + \frac{1}{2}) a_0}{\sqrt{3} Z'} . \tag{14}$$

(iii) The CNDO approximation can be formally justified by regarding the basis orbitals as approximations to the Löwdin orbitals [10]

$$\bar{\phi} = \phi S^{-1/2} . \tag{15}$$

Dixon [11] has suggested that the dipole moment be calculated with reference to the Löwdin basis. The dipole integrals are the matrix elements of a one-electron operator, so that in the Löwdin basis, the X-matrix is transformed to [10]

$$\bar{X} = S^{-1/2} X S^{-1/2} \tag{16}$$

and dipole moment is transformed to

$$\bar{\mu}_x = -e\,\mathrm{tr}\,\boldsymbol{P}\bar{X} + e\sum_{\mathrm{A}} Z_{\mathrm{A}} X_{\mathrm{A}} = -e\,\mathrm{tr}(\boldsymbol{P}S^{-1/2} X S^{-1/2}) + e\sum_{\mathrm{A}} Z_{\mathrm{A}} X_{\mathrm{A}}\,. \tag{17}$$

Equation (17) is invariant under a change of origin, since the Löwdin basis is orthogonal.

In this paper, all three methods are used to calculate dipole moments from the SCF-MO theory, and the results are compared with experimental dipole moments determined from microwave spectroscopy. All computed dipole moments are multiplied by the conversion factor 4.80294 from atomic units to Debyes, for comparison with experimental values.

C. Comparison of Calculated Dipole Moments with Experiment for First Row Molecules

The different formulae for the calculation of dipole moments in a molecular orbital theory with neglect of overlap are compared in Table 1 for the wave functions computed from the semi-empirical SCF-MO-CNDO theory, with the parameters which were shown to be the best for the prediction of ionization potentials

Table 1. *Comparison of methods of calculation of dipole moments*[a] *for first-row molecules from* SCF-MO-CNDO *theory with empirical atomic and bonding parameters*

Calculation of μ	Point-charge		Pople and Segal		Dixon		Exptl.	Ref.
Interatomic Repulsion integral[d]	$M2$	$O2$	$M2$	$O2$	$M2$	$O2$		
LiH	4.083	6.030	6.699	7.218	7.024	7.479	5.882 D	[18]
H_3N	0.465	0.962	1.973	2.221	0.643	0.991	1.468	[19]
H_2O	0.876	1.417	1.803	2.175	0.929	1.391	1.87	[20]
HF	1.397	1.866	1.899	2.265	1.578	2.003	1.8195	[21]
CO	1.549	2.097	0.789	1.372	1.308	2.017	−0.112	[22, 23]
NNO		0.838		0.601		0.862	0.166	[24]
O_3[b]	0.734	0.893	0.876	0.909	0.429	0.583	0.58	[25]
C_3H_8[c]	0.183	0.106	0.084	0.041	0.151	0.082	0.083	[26]
LiF	6.052	6.818	6.602	7.098	6.833	7.222	6.328	[27]
CH_3F	2.721	2.812	2.647	2.687	2.391	2.408	1.8555	[28]
HCN	1.582	1.689	3.015	2.946	1.547	1.501	2.985	[29]
CH_3CN		2.440		3.709		2.173	3.92	[30]
FCN	−0.667	−0.427	0.482	0.648	−0.364	−0.165	2.17	[31]

[a] Positive sign indicates polarity A^+B^-, where A is first atom written.

[b] Positive sign indicates central oxygen at positive end.

[c] Positive sign indicates central carbon at positive end.

[d] $M2$ and $O2$ are retained to make table consistent with Part III (Ref. [1b]) and signify that the formulae of Mataga and Ohno with $Z'_H = 1.2$ have been used in the calculations.

and bonding energies [1a, 1b]. The point-charge formula is in overall poor agreement with experiment, showing that the prediction of accurate dipole moments requires the inclusion of atomic polarization effects. The results obtained with the Pople-Segal formula show that the inclusion of these effects does lead to substantial improvement of the results, although they are still not very accurate for some molecules. The dipole moments computed from the Dixon formula, using Löwdin orbitals as a basis, are less accurate on the whole, than those calculated from the Pople-Segal formula. The Pople-Segal formula is, therefore, the best for the calculation of approximate dipole moments, and the errors in the results may be mostly due to errors in the wave function, rather than in Eq. (13).

Table 1 also shows that the computed dipole moment is quite sensitive to changes in the interatomic electron-repulsion integrals. The Mataga formula leads to more accurate dipole moments, as computed by the Pople-Segal formula, than the Ohno formula, for all the molecules considered except FCN. This is evidence in favour of the Mataga formula, although only a few of the computed dipole moments are accurate enough to be used as evidence.

Dipole moments of first-row molecules, calculated by the Pople-Segal formula, using the different sets of parameters for the SCF-MO-CNDO theory, are shown in Table 2. The values of the electron-repulsion integrals have a substantial effect on dipole moments, since they determine the potential energy corresponding to a given charge distribution, which in turn determines the self-consistent charge distribution. Dipole moments, like ionization potentials, are relatively unaffected

Table 2. *Dipole moments*[a] *of first-row molecules calculated as per Pople and Segal from* SCF-MO *theory and* CNDO *approximation, and from the Extended Hückel Theory*

Parameter set	*M2*	*MP*	*O2*	*OP*	*R2*	*RP*	*H2*	Exptl.
LiH	6.699	6.218	7.218	6.284	6.365	6.192	7.292	5.882
H_3N	1.973	2.212	2.221	2.382	1.873	2.104	2.471	1.468
H_2O	1.803	2.190	2.175	2.378	1.784	2.142	3.737	1.87
HF	1.899	1.929	2.265	2.037	1.741	1.849	3.615	1.8195
CO	0.789	−1.113	1.372	−1.510	0.547	−0.961	3.232	−0.112
NNO		0.227	0.601	−0.300	0.454	0.761	1.880	0.166
O_3	0.876	1.197	0.909	1.680		1.178	3.444	0.58
C_3H_8	0.084	0.019	0.041	−0.005	0.003	−0.001	0.010	0.083
LiF	6.602	4.926	7.098	4.934	5.936	5.079	7.499	6.328
CH_3F	2.647	1.780	2.687	1.699	1.943	1.719	4.071	1.8555
HCN	3.015	2.993	2.946	3.094	2.581	2.463	7.307	2.985
CH_3CN		3.977	3.709	4.160		3.053	8.797	3.92
FCN	0.482	2.457	0.648	3.004	0.908	1.704	4.845	2.17

[a] Sign convention as in Table 1.

M: Mataga interatomic γ_{AB}.

O: Ohno interatomic γ_{AB}.

R: Theoretical interatomic γ_{AB} of Roothaan.

H: Extended Hückel Theory [6].

2: Hydrogen exponent Z'_H is 1.2.

P: Bonding parameters β_A^0 derived from Pople and Segal [4].

References as in text.

by changes in the Slater exponent for hydrogen, so that the results for $Z'_H = 1.0$ are not explicitly shown in this paper.

For some molecules, the dipole moments computed using the Pople-Segal bonding parameters are quite different from those computed using the empirical bonding parameters. This can be explained by considering the dependence of the molecular energy on the bonding parameters in the SCF-MO-CNDO theory. The energy eigenvalue of the electronic Hamiltonian has the form,

$$E_e = \frac{1}{2} \sum_{k,l} P_{kl}(F_{kl} + H_{kl}) . \tag{18}$$

If the bonding parameters are increased, the interatomic matrix elements H_{kl} and F_{kl} are increased in magnitude, so that the molecule can attain a lower energy by increasing the interatomic P_{kl}, i.e., by the transfer of electron density from lone-pair orbitals into bonding orbitals. The large changes in dipole moment can be explained in terms of this effect. For LiF and CH_3F, the decrease in dipole moment with increased bonding parameters is due to a transfer of electron density from the fluorine lone-pair orbitals to the bonding orbitals. In HF, examination of the population matrix shows that this effect is cancelled by an increase in the atomic polarization of the fluorine atom. For FCN, the transfer of electron density away from the fluorine nucleus leads to an increase in the computed dipole moment, since the polarity of the molecule is $\mathrm{F}\overset{+}{\mathrm{C}}\overset{-}{\mathrm{N}}$. For CO, the increase in bonding parameters results in enough charge transfer to reverse the polarity of the computed dipole moments.

Column $H2$ shows that the Extended Hückel Theory greatly exaggerates the polarities of all molecules considered except propane. In the SCF-MO-CNDO theory, the accumulation of electron density on the more electronegative atom is limited by the electrostatic repulsion of the electrons for each other. This is not so in the EHT, since the Hamiltonian matrix elements are independent of the molecular charge distribution, and do not include electron-repulsion terms. The SCF-MO-CNDO theory predicts more accurate dipole moments than the EHT, regardless of the choice of parameters, and even though the dipole moment must be computed approximately, in order to preserve translational invariance. This shows that the SCF-MO-CNDO theory is a definite improvement over the EHT, in spite of the uncertainties in some of the parameters.

The above conclusions about the accuracy of computed dipole moments are supported by other recent calculations. Pople and Gordon [12] have calculated the dipole moments of a number of organic molecules from the SCF-MO-CNDO theory with theoretical electron-repulsion integrals and Pople-Segal bonding parameters (Parameter set RP). The overall accuracy of their results is comparable to that for the molecules considered here, and they have used the results as the basis for an analysis of substituent effect in dipole moments.

As for the Extended Hückel Theory, the dipole moments of heterocyclic molecules calculated by Adam and Grimison [13] are much larger than experimental values, as for the small molecules considered here. A similar conclusion about the inadequacy of the charge distributions in the EHT, due to the absence of electron-repulsion terms in the Hamiltonian matrix elements, was previously based on an attempt to correlate the gross atomic charges of the EHT with chemical shifts [14], and on a comparison of the computed charge distribution with those obtained from electronegativity equalization theory [15, 16]. This conclusion is now more firmly based on the predicted values of a molecular property, the dipole moment, which is calculated directly from the ground-state wave function.

D. Comparison of Calculated Dipole Moments with Experimental for Molecules Containing Non-First-Row Atoms

Dipole moments, calculated from both the SCF-MO-CNDO theory (using the Pople-Segal formula) and the Extended Hückel Theory, are listed in Table 3 for molecules containing atoms not in the first row of the periodic table. The EHT predicts exaggerated polarities as for first-row molecules, but now the SCF-MO-

Table 3. *Calculated dipole moments*[a] *for molecules including non-first row elements from* SCF-MO *theory,* SCF-MO-CNDO *theory and the Extended Hückel Theory*

Calculation of μ $Z'_H = 1.2$ Interatomic	Point-charge		SCF-MO-CNDO including *sp*-polarization		Extended Hückel	Dixon		Exptl.	Ref.
Repulsion integral	*M2* Mataga	*O2* Ohno	*M2* Mataga	*O2* Ohno	*H2*	*M2*	*O2*		
H_3P	−0.127	−0.344	2.379	1.906	1.482	0.827	0.260	0.578 D	[22]
H_3As	−0.064	−0.259	2.908	2.427	0.257	1.286	0.712	0.22	[32]
H_3Sb	−0.351	−0.796	2.587	1.863	−0.834	0.707	−0.120	0.116	[32]
H_2S	0.408	0.576	2.152	2.100	2.957	0.985	0.932	0.974	[33]
H_2Se	0.648	0.961	2.565	2.627	2.652	1.340	1.435	0.24, 0.62	[34, 35]
H_2Te	0.662	0.930	2.789	2.817	1.958	1.503	1.550		
HCl	1.006	1.296	2.002	2.180	3.477	1.453	1.650	1.12	[36]
HBr	0.727	0.919	1.813	1.865	3.232	1.050	1.122	0.83	[36]
HI	0.548	0.659	1.979	1.934	3.113	1.154	1.109	0.445	[36]
CS	1.234	1.410	1.614	1.460	−3.564	1.406	1.869	1.97	[37]
OCS	−0.891	−1.108	0.241	0.028	−3.609	−0.448	−0.766	0.7124	[38]
SO_2	1.633	2.919	1.273	2.190	6.219	0.179	1.548	1.59	[39]
ClF	1.412	1.780	0.962	1.386	3.166	0.977	1.401	0.881	[40]
BrF	2.160	2.710	1.636	2.260	4.106	1.668	2.292	1.29	[41]
BrCl	0.744	0.925	0.646	0.835	−5.712	−3.644	−3.143	0.57	[42]
IF	2.859	3.481	2.113	2.841	6.028	2.248	2.969		
ICl	1.188	1.441	0.736	1.021	1.843	0.833	1.123	0.65	[43]
IBr	0.452	0.552	0.109	0.233	0.535	0.126	0.253		
CH_3Cl	2.101	2.104	2.667	2.588	3.635	2.327	2.235	1.869	[24]
CH_3Br	1.697	1.649	2.436	2.304	3.205	1.994	1.847	1.797	[24]
CH_3I	1.387	1.287	2.496	2.297	3.178	1.998	1.781	1.647	[24]
ClCN	0.383	0.498	0.922	1.014	7.232	−0.109	−0.036	2.802	[24]
BrCn		1.094		1.412	8.700		0.506	2.94	[31]
ICN	1.287	1.462	1.210	1.365	8.636	0.415	0.598	3.71	[31]

[a] Sign convention as in Table 1.

M: Mataga interatomic γ_{AB}.

O: Ohno interatomic γ_{AB}.

H: Extended Hückel Theory

2: Hydrogen exponent Z'_H is 1.2.

References as in text.

CNDO theory also predicts dipole moments which are much higher than the experimental ones, and in some cases higher than those from the EHT. The calculations, as in earlier papers [1a, 1b] include only *s* and *p* valence shell orbitals in the basis set. The fact that the dipole moments are much less accurate than those calculated using the same theory for molecules containing only first row elements may be due to the absence of *d*-orbitals in the basis set. Santry and Segal [9] included *d*-orbitals in the SCF-MO-CNDO theory for second row elements using theoretical repulsion integrals and theoretical bonding parameters [4] and obtained slightly better dipole moments.

Table 3 also shows that the point charge term is a better approximation than the semi-empirical SCF-MO-CNDO results for many molecules, as are the results from using the Dixon formula.

E. Conclusion

The semi-empirical SCF-MO-CNDO theory can thus be used to calculate approximate dipole moments with comparable accuracy to those obtained using theoretical parameters. For molecules containing second row elements the semi-empirical theory apparently requires the inclusion of *d*-orbitals as does the SCF-MO-CNDO theory with theoretical parameters [9, 14]. The EHT predicts exaggerated dipole moments in most molecules. Much work remains to be done in developing empirical parameters for *d*-orbitals and in predicting dipole moments.

Acknowledgments. This research was supported by the National Research Council of Canada to whom IMS is grateful for Scholarships (1964—1967). The McGill Computing Centre provided facilities.

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