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On the Calculation of Molecular Dipole Moments

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The approximation made in the calculation of molecular dipole moments by including only the point charges and the atomic dipoles is evaluated in different all-valence (or all)-electrons MO procedures. In the CNDO method, the use of the exact formula after retransformation of the atomic basis into Slater orbitals gives poorer values than the Pople-Segal's procedure.

It has become customary when using "non *ab initio*" methods, to calculate molecular dipole moments in the point-charge approximation, correcting it, at best, by addition of a "hybrid moment" so as to take into account the asymmetry of the atomic charge clouds. This last procedure has known a renewed favor lately [1] and has been extensively used for the evaluation of the dipole moments of heteromolecules [2–5] calculated by the recently developed all-valence-electrons techniques [1, 6–10].

In fact, when all the valence electrons are explicitely introduced in a molecular calculation there is no reason for not using the exact expression of the dipole moment since the necessary integrals can be nowadays easily computed using master formulas of diverse sources [11, 12]. For a molecule represented by a Slater determinant built on doubly occupied LCAO molecular orbitals:

$$\varphi_i = \sum_\nu c_{i\nu} \chi_\nu \qquad (1)$$

the component of the molecular moment along a given axis x can be expressed [13] in terms of the coefficients of the atomic orbitals χ_ν, of the nuclear (or core) charges and coordinates Z_R and x_R and of dipole moment integrals

$$x_{\nu\mu} = \int \chi_\nu x \chi_\mu d\tau \qquad (2)$$

by:

$$\mu_x = \sum_{\nu,\mu} P_{\nu\mu} x_{\nu\mu} - \sum_R Z_R x_R \qquad (3)$$

where

$$P_{\nu\mu} = \sum_i 2 c_{i_\nu} c_{i_\mu} . \qquad (4)$$

This may be conveniently rewritten as a summation over all atoms R of atom contributions:

$$\mu_x^R = x_R \left[\sum_\nu^R P_{\nu_R \nu_R} - Z_R \right] + \sum_\nu^R \sum_{\mu \neq \nu}^R P_{\nu_R \mu_R} x_{\nu_R \mu_R} + \sum_\nu^R \sum_\mu^{S \neq R} P_{\nu_R \mu_S} x_{\nu_R \mu_S} . \qquad (5)$$

On the other hand, in the point-charge approximation when the gross atomic populations of Mulliken are used as point charges, the corresponding contribution to μ_x for atom R is:

$$\bar{\mu}_x^R = x_R \left[\sum_\nu^R P_{\nu_R \nu_R} - Z_R \right] + x_R \left[\sum_\nu^R \sum_\mu^{S \neq R} P_{\nu_R \mu_S} S_{\nu_R \mu_S} \right] . \qquad (6)$$

The first term in (5) is the same as in (6). The second term in (5) has no analog in (6): it is the "hybrid moment" for atom R [15], the summation of which over all atoms yields the total hybrid moment μ_{sp} introduced by Pople and Segal [1] as a correcting term to the moment calculated by the point-charge approximation. Finally the third term in μ_x^R involves the integral $x_{\nu_R \mu_S}$ which may be written in term of the homopolar dipole integral proper $\xi_{\nu_R \mu_S}$ defined by Mulliken [14] and Coulson [15] in the diatomic case:

$$x_{\nu_R \mu_S} = \tfrac{1}{2} S_{\nu_R \mu_S}(x_R + x_S) + \xi_{\nu_R \mu_S} \tag{7}$$

with

$$\xi_{\nu_R \mu_S} = \int \chi_{\nu_R} \xi \chi_{\mu_S} d\tau \tag{8}$$

where ξ is the coordinate parallel to x refered to a system of local axis centered in the middle of the bond RS.

Thus, the calculation of the dipole moment in the point-charge approximation can be made equivalent to the exact calculation by adding not only the hybrid moment but also the total "homopolar dipole" contribution:

$$\mu_{\text{h.d.}} = \sum_R \sum_{S \neq R} \sum_{\nu}^{R} \sum_{\mu}^{S} P_{\nu_R \mu_S} \xi_{\nu_R \mu_S} . \tag{9}$$

In order to investigate the numerical importance of the approximation made in the calculation of the dipole moment by including only the point charges and the atomic dipoles we undertook the exact calculation of the dipole moment of some molecules. For the programmation of the computation of the exact dipole moments integrals we followed the formulas developed by Hamilton [11] for integrals over Slater orbitals.

A first investigation was made for formaldehyde, pyrrole and pyridine, utilizing eigenvectors obtained by CNDO/2. But in this case the addition of the two-center terms given by (9) can be made at two levels of approximation. First it is possible just to add the $\xi_{\nu_R \mu_S}$ terms to the dipole moment computed by the Pople-Segal procedure. On the other hand, since the CNDO eigenvectors are obtained in the zero differential overlap approximation, they can, according to Pople and Segal [1] who follow a nearly suggestion by Fumi and Parr [16] and McWeeny [17] be thought of as expressed in terms of orthogonalized orbitals derived from Slater orbitaly by the Löwdin [18] transformation. If this assumption is retained one must in order to calculate the exact dipole moment either transform the complete dipole moment matrix so as to express it directly over orthogonalized atomic orbitals (this procedure was adopted by Dixon [19] with EMZDO eigenvectors for H_2O, NH_3 and H_2CO) or retransform the CNDO orthogonal orbital coefficients into Slater orbital coefficients by the matrix product

$$C^{\chi} = S^{-1/2} C^{\lambda} .$$

We chose the last procedure for two reasons. The other existing all-valence electron theories, of the extended-Hückel type, as well as non-empirical methods using Slater or Gaussian atomic orbitals always give gross atomic populations, whereas CNDO computes net populations[1]; so it was not without interest to study the numerical effect of the transformation on the computed electronic distribution. In addition by this procedure we are able to separate the effect

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[1] For the definition of the populations in the different basis sets we follow Mulliken's notation [20].

of the change of basis set and the effect of the introduction of the two center integrals on the calculated value of the dipole moments.

The gross atomic charges obtained after the transformation are given in Fig. 1. The λ net atomic charges are given for comparison. It is seen that the π charges are practically unchanged but the σ charges are modified by a larger quantity. The transformation makes the hydrogen atoms more positive and the electronegative atoms like N or O more negatively charged. The σ charges so obtained are now closer to those calculated by Berthod at Pullman [21] using Del Re's modified method or by other semiempirical all-valence electrons methods like EHT or IEHC [4].

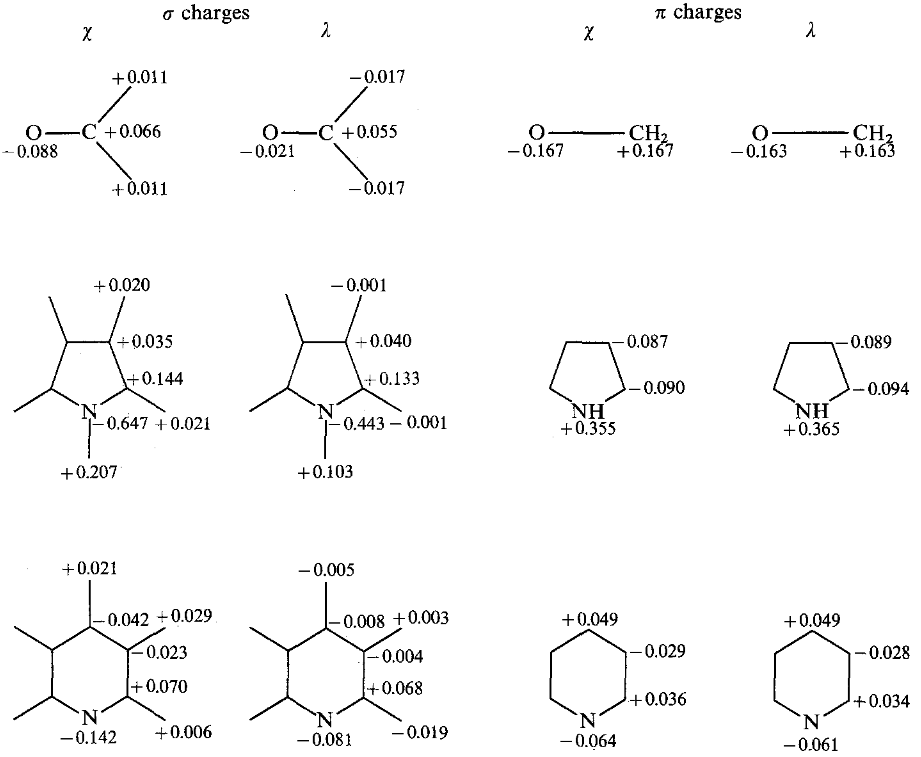

Fig. 1. CNDO/2 net charges (λ: as defined in [1, 6, 7, 2], χ: in a Slater basis set)

As to the dipole moments, Table 1 gives the calculated values at different levels of approximation: for each molecule the first line gives the dipole moment calculated according to Pople and Segal's procedure [1] with no modification. The second line gives the same quantities simply supplemented with the $\xi_{\mu\nu}$ contributions (overlap neglected). The third line gives the value corresponding to line one but reevaluated in the χ basis. The fourth line gives the dipole moment calculated exactly with all the two-center integrals. From column four we see that the π dipole moment is not very sensitive to the way the net charges are evaluated, neither to the introduction of all the integrals. On the contrary, the

σ contribution to the dipole moment is more strongly modified in the cases we examined. The exact calculation using CNDO/2 wave functions leads to numerical values less in accord with experiment than the ones evaluated with the ponctual charges plus the atomic dipoles in the orthogonal basis.

Table 1. *Dipole moments in Debye units*[a]

Molecule	Method		μ_{Q_σ}	μ_{sp}	μ_σ	μ_π	$\mu_{Q_\sigma+\pi}$	μ_{tot}
Formaldehyde	approximate	$\lambda(1)$	0.02	0.92	0.94	0.95	0.97	1.89
		$\lambda(2)$			-0.39	1.22		0.84
		χ	0.57	1.55	2.12	0.97	1.54	3.09
	exact				0.43	1.20		1.63
	experimental [26]							2.34
Pyrrole	approximate	$\lambda(1)$	1.31	-0.78	0.53	-2.52	-1.21	-1.99
		$\lambda(2)$			-0.12	-2.44		-2.57
		χ	1.50	0.15	1.65	-2.45	-0.95	-0.80
	exact				1.43	-2.43		-1.0
	experimental [26]							1.8
Pyridine	approximate	$\lambda(1)$	0.22	1.60	1.80	0.33	0.55	2.15
		$\lambda(2)$			0.03	0.44		0.46
		χ	0.58	1.38	1.96	0.33	0.91	2.29
	exact				1.04	0.41		1.44
	experimental [26]							2.2

[a] μ_Q: moment due to the point-populations only. μ_{sp}: total hybrid moment. Axis directed towards O, NH, or N. – $\lambda(1)$: Pople and Segal's procedure. $\lambda(2)$: as $\lambda(1)$ plus $\xi_{\nu_R \mu_S}$ terms.

Table 2. *Dipole moment of formaldehyde in Debye units calculated with different wave functions (experimental value: 2,34 D)*

MO-Method	Calculation of μ	σ	π	Total
EHT[a]	approximate[b]	3.58	4.71	8.29
	exact	2.59	4.81	7.40
IEHC[a]	approximate[b]	2.44	0.83	3.27
	exact	0.77	1.06	1.83
Non empirical	approximate[b]	2.70	-0.18	2.52
Newton and Palke [22]	exact	0.94	0.06	1
CNDO	approximate[b]	2.12	0.97	3.09
	exact	0.43	1.20	1.63

[a] EHT: extended Hückel, IEHC: iterative extended Hückel used as in Ref. [4].

[b] This line corresponds in all the cases to a calculation made according to Pople and Segal's procedure buth with Slater atomic orbitals in order to make all four calculations more comparable.

In fact one may wonder if the decrease of the sigma component of the computed dipole moment that we obtain when we take into account the $\xi_{\mu_R \nu_S}$ terms are due to the defects inherent to the use of the CNDO/2 eigenvectors. Thus we have calculated for formaldehyde approximate and exact dipole moments using three other different wave functions aside from the CNDO/2 already given: extended Hückel theory, iterative extended Hückel, and the non-empirical wave function B computed by Newton and Palke [22]. For the four calculations we obtain a marked decrease in the dipole moment when we include the bicentric integrals. Both our theoretical analysis and these numerical results seem to indicate that this decrease is due to the CH homopolar or overlap dipole: Coulson and Rogers [12] have shown that these homopolar dipoles for a purely covalent CH bond have a value as large as 1 Debye and, in the present case, they substract from the approximate dipole. This contention seems supported by the small differences between the exact and point-charge values of the calculated moment in methyl acetylene [23] as well as by the data of Table 1 for pyrrole where compensation of the CH dipoles seems to occur in the Slater basis set while this does not happen in pyridine.

This exploratory investigation shows that the effect of including all the two-center integrals is qualitatively the same in all procedures and affects strongly the σ component of the dipole moment. There is no doubt that the use of the exact formulation is the most logical attitude at least in procedures which retain overlap like EHT or IEHC and the fact that the IEHC "exact" calculation in H_2CO yields a nearly satisfactory moment deserves further exploration. The non-iterative EHT "exact" result is still far from being small enough as was to be expected on account of the strong exaggeration of the charge displacements in this procedure [4].

As to the CNDO-results, they appear less good in the "exact" formulation than in the original procedure with no retransformation of the basis. It may of course be objected that this de-orthogonalization of the basis, however intellectually satisfactory it seems, is not really rigorous on account of the approximations involved in the procedure, but the similarity of effects observed in Table 2 between CNDO and *ab initio* calculations suggests that in both cases, the limits in accuracy on the dipole moment are imposed by the minimal and non-optimized character of the Slater basis set (recent studies tend to indicate that minimal basis sets do not suffice for obtaining good values of dipole moments [24, 25].

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