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## New basis set for molecular calculations II. A CNDO study of electric dipole moments and electronic valence population on AH and AB systems using the modified Slater orbitals.

B J Costa Cabral † and J D M Vianna‡

† Instituto de Física, Universidade Federal da Bahia, Campus Federação, 40 000 Salvador Ba, Brazil

‡ Departamento de Física, Instituto de Ciências Exatas, Universidade de Brasília, 70 910 Brasília DF, Brazil

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**Abstract.** The modified Slater orbitals (MSO) basis set is utilised in calculation of the electronic valence population and the electric dipole moments in AH and AB systems, A and B being a second-row elements (from B to F). The Hartree–Fock–Roothaan equations are solved using the CNDO/BW method. The resonance integrals are evaluated with and without the inclusion of valence state ionisation potentials. It is shown that going from the Slater to modified Slater orbitals basis sets there is a systematic charge transfer to the lighter element in a diatomic system. For electric dipole moments, the results using the MSO are comparable with *ab initio* calculations and better than CNDO/2 results and CNDO/BW results with the Slater basis set.

### 1. Introduction

The most generally used atomic orbital basis set for expansion of molecular orbitals in LCAO–MO–SCF methods is the well known Slater-type orbitals (STO) basis set. However, it is known that there are many discussions about to which orbitals the CNDO (and INDO) equations actually correspond best. In order to test the modified Slater orbitals (MSO) (Shibuya 1973) in CNDO calculations, Canuto and Vianna (1975) studied bonding energies, equilibrium geometries, molecular orbital energies and force constants for  $AH_n$ -type molecules ( $A = F, O, N, C, B; n = 1, 2, 3$ ). Their results showed that the values calculated using the MSO are better than the CNDO results with a Slater basis set, and encouraged the present study of the electric dipole moments of AH and AB ( $A, B = F, O, N, C, B$ ) systems. Our attention in the present paper is limited to diatomic molecules because of the greater availability of accurate experimental and theoretical values. As in Canuto and Vianna (1975), hereafter referred to as I, in order to solve the Hartree–Fock–Roothaan equations (Roothaan 1951) we use the CNDO–SCF–MO method which was originally suggested by Pople *et al* (1965) and which includes all the valence electrons irrespective of their type. The parametrisation we adopted is that of the CNDO/BW-type (Boyd and Whitehead 1972) with valence state energies given by Hinze and Jaffé (1962). As in I, we use an sp MSO basis set and two distinct formulae to

calculate off-diagonal Hartree–Fock matrix elements, i.e.

$$F_{\mu\nu} = -\beta_{AB}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \quad (1)$$

$$F_{\mu\nu} = -\beta'_{AB}(I_{\mu} + I_{\nu})S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB}. \quad (2)$$

In equation (2) the valence state ionisation potentials (VSIP)  $I_{\mu}$  of Hinze and Jaffé (1962) are used. In all calculations reported here, the bond lengths were varied until the most stable configuration was found. For open-shell molecules the unrestricted single determinant (different orbitals for different spins) was used throughout.

In § 2 we present a résumé about electric dipole moments of molecular systems. In § 3 our results are compared with the experimental values and those obtained from *ab initio* and CNDO/2, CNDO/BW methods with Slater orbitals.

## 2. Electric dipole moments

For a molecule represented by a Slater determinant built on occupied LCAO molecular orbitals

$$\phi_i = \sum_{\nu} C_{i\nu}\chi_{\nu}$$

the molecular dipole moment can be expressed in terms of the coefficients of valence atomic orbitals  $\chi_{\nu}$ , of the nuclear core charges and position vectors  $Z_A$  and  $r_A$ , and of dipole moment integrals

$$r_{\mu_A\nu_B} = \int \chi_{\mu}^A r \chi_{\nu}^B d\tau$$

by (Giessner-Pretter and Pullman 1968)

$$\begin{aligned} \mu = e \sum_A (Z_A - P_{AA})r_A - e \sum_A \sum_{\mu \neq \nu} P_{\mu_A\nu_A} r_{\mu_A\nu_A} - e \sum_{A \neq B} \sum_{\mu} P_{\mu_A\nu_B} r_{\mu_A\nu_B} \\ - e \sum_{A \neq B} \sum_{\mu \neq \nu} P_{\mu_A\nu_B} r_{\mu_A\nu_B} \end{aligned} \quad (3)$$

where

$$P_{AA} = \sum_{\mu \in A} P_{\mu\mu}$$

$$P_{\mu\nu} = \sum_i N(i) C_{i\mu} C_{i\nu}$$

$N(i)$  being the electron occupation number of the molecular orbital  $\phi_i$ .

In the CNDO approximation with an sp basis set, the molecular dipole moments are obtained as a sum of two parts (Pople and Segal 1965),

$$\mu_{\text{CNDO}} = \mu_Q + \mu_e \quad (4)$$

where

$$\mu_Q = e \sum_A (Z_A - P_{AA})r_A \quad (5)$$

is the contribution from the net atomic charge densities, and

$$\mu_c = -e \sum_A \sum_{\mu \neq \nu} P_{\mu_A \nu_A} r_{\mu_A \nu_A}$$

is the contribution from atomic polarisation resulting from mixing of the  $S_A$  and  $P_A$  orbitals.

In the present paper, the relations (3), (4) and (5) are used to calculate dipole moments. The equation (3) is utilised with the Löwdin basis (Löwdin 1950) as Dixon (1967) has suggested, and with the MSO basis set; the corresponding relations we denote by  $\mu_{\text{DIXON}}$  and  $\mu_{\text{SH}}$  respectively. The equations (4) and (5) are used with both the STO and the MSO basis functions. In fact, by comparing the values of  $\mu_{\text{CNDO}}$ ,  $\mu_{\text{Q}}$ ,  $\mu_{\text{DIXON}}$  and  $\mu_{\text{SH}}$  it is possible to obtain the atomic and interatomic contributions for the molecular dipole moment.

In all our calculations the resonance integrals were evaluated with and without the inclusion of valence state ionisation potentials. The dipole moment integrals  $r_{\mu_A \nu_B}$  were calculated using Mulliken's method (Mulliken *et al* 1949).

### 3. Results and discussion

Tables 1 and 2 summarise our results for charge distributions and dipole moments.

#### 3.1. Charge distributions

Table 1 gives the result of the electronic valence population (EVP) analysis. Our results indicate that the EVP is significantly modified by changing the STO to MSO; the

**Table 1.** Electronic valence populations (EVP) calculated using equations (1) and (2).

Molecule	LCAO basis set	STO		MSO	
	$P_{AA}$	(1)	(2)	(1)	(2)
FH	$P_{HH}$	0.6006	0.5302	0.6566	0.6000
	$P_{FF}$	7.3994	7.4698	7.3434	7.4000
CH	$P_{HH}$	1.0375	0.9820	1.0594	1.0227
	$P_{CC}$	3.9625	4.0180	3.9406	3.9773
BH	$P_{HH}$	1.1790	1.1486	1.1848	1.1638
	$P_{BB}$	2.8210	2.8514	2.8152	2.8362
HN	$P_{HH}$	0.8111	0.7509	0.8508	0.8099
	$P_{NN}$	5.1889	5.2491	5.1492	5.1901
OH	$P_{HH}$	0.7140	0.6477	0.7637	0.7182
	$P_{OO}$	6.2860	6.3523	6.2363	6.2818
CN	$P_{CC}$	3.7508	3.7145	3.9274	3.9224
	$P_{NN}$	5.2492	5.2855	5.0726	5.0776
BF	$P_{BB}$	2.6500	2.5934	3.1272	3.0559
	$P_{FF}$	7.3500	7.4066	6.8728	6.9941
CO	$P_{CC}$	3.7220	3.6864	3.9048	3.8312
	$P_{OO}$	6.2780	6.3136	6.0952	6.1688
NO	$P_{NN}$	4.8949	4.8822	5.0820	5.0595
	$P_{OO}$	6.1051	6.1178	5.9180	5.9405

modifications are greater in AB than in AH systems. For the diatomic systems studied it is observed that going from STO to MSO basis functions, the effect of including valence state ionisation potentials in the evaluation of the resonance integrals is relatively small. A similar result has been pointed out by Boyd and Whitehead (1972) with reference to the STO basis set in the calculations of bonding energies, equilibrium geometries and force constants.

### 3.2. Dipole moments for AH systems

The results reported in the table 2 show that in the present study the best results for the electric dipole moment for NH, OH and FH are obtained with the MSO basis set and equation (2). For BH and CH the values using STO are better than those evaluated with MSO. The results obtained by the using  $\mu_{\text{DIXON}}$  and  $\mu_{\text{SH}}$  are not in agreement with the experimental data. The dipole moments  $\mu_{\text{CNDO}}$  evaluated from equations (1) and (2) and the MSO are systematically lower than the corresponding values obtained with the STO basis functions. It happens mainly because the MSO contribution  $\mu_e$  in the equation (4) is lower than the STO one. The inclusion of valence state ionisation potentials in the evaluation of  $F_{\mu\nu}$  results in  $\mu_{\text{CNDO}}$  values greater than without the inclusion of the valence state ionisation potential in both the MSO and the STO basis functions.

### 3.3 Dipole moments for AB systems

For the AB systems table 2 demonstrates that the values with the MSO basis set are not good. The *ab initio*, CNDO/BW with the STO basis functions and the CNDO/2 results, however, are also in very poor agreement with the experimental data; in fact, by comparing the several results it is observed that the best value for BF is obtained by  $\mu_{\text{SH}}$ , and the best values for CN and CO are obtained from  $\mu_{\text{CNDO}}$  using the MSO basis set. It is also observed that for CN and NO the MSO contributions from interatomic and atomic polarisation are greater than the corresponding STO contributions. For BF and CO the converse is true.

## 4. Conclusions

The modified Slater orbitals basis set has been used in the calculation of electric dipole moments and electronic charge distributions for AH and AB systems. The CNDO/BW method was utilised to solve the Hartree–Fock–Roothaan equations. Our results show that in the MSO basis  $\mu_{\text{CNDO}}$  values calculated with equation (2) are better (the mean deviation from experiment is 0.618 D) than the  $\mu_{\text{CNDO}}$  results evaluated with equation (1) (where the mean deviation from experiments is 0.807 D). For the set of molecules considered and using equation (2) the MSO give dipole moments which are:

- (i) better than CNDO/2 results (mean deviation from experiments: 0.832 D) and CNDO/BW results with a Slater basis set (mean deviation from experiment: 0.789 D)
- (ii) comparable with *ab initio* calculations (Green 1975) (mean deviation from experiment: 0.420 D)

The MSO contributions from atomic polarisation are, excluding CN and NO, systematically lower (in absolute values) than the corresponding STO contributions. For the contributions from interatomic polarisation, excluding BF and CO, the inverse is true. Going from the Slater to modified Slater orbitals basis sets there is a systematic

charge transfer to the lighter element in a diatomic system. The inclusion of vsIP in the evaluation of resonance integrals generally predicts, in the MSO basis, greater dipole moments than the simple overlap proportionality.

**Table 2.** A comparison of electric dipole moments (in debye) calculated with equations (1) and (2) and the experimental values.

Theor. method.		CNDO/BW				CNDO/2 <sup>c</sup>		
LCAO basis set		STO		MSO				
Molecule		(1)	(2)	(1)	(2)			
FH	$\mu_Q$	1.761	2.071	1.552	1.837			
	$\mu_{\text{CNDO}}$	2.309	2.721	1.682	2.001	1.86		
	$\mu_{\text{DIXON}}$	2.013	2.723					
CH	$\mu_{\text{SH}}$			-2.091	-1.995			
	$\mu_Q$	-0.200	0.095	-0.326	-0.124			
	$\mu_{\text{CNDO}}$	1.206	1.775	0.086	0.383	1.87		
BH	$\mu_{\text{DIXON}}$	-0.203	0.823					
	$\mu_{\text{SH}}$			-4.454	-4.474			
	$\mu_Q$	-1.042	-0.860	-1.122	-0.986			
NH	$\mu_{\text{CNDO}}$	1.012	1.510	-0.431	-0.176	-2.13		
	$\mu_{\text{DIXON}}$	-0.708	-0.018					
	$\mu_{\text{SH}}$			-5.444	-5.458			
OH	$\mu_Q$	0.913	1.213	0.739	0.955			
	$\mu_{\text{CNDO}}$	1.784	2.301	0.973	1.257	1.76		
	$\mu_{\text{DIXON}}$	0.975	1.843					
CN	$\mu_{\text{SH}}$			-3.641	-4.571			
	$\mu_Q$	1.308	1.624	1.107	1.347			
	$\mu_{\text{CNDO}}$	1.987	2.466	1.276	1.566	1.78		
BF	$\mu_{\text{SIXON}}$	1.437	2.251					
	$\mu_{\text{SH}}$			-2.781	-2.684			
	$\mu_Q$	-1.376	-1.584	-0.352	-0.386			
CO	$\mu_{\text{CNDO}}$	-1.177	-1.160	0.265	0.402	0.85		
	$\mu_{\text{DIXON}}$	-1.666	-1.806					
	$\mu_{\text{SH}}$			-6.380	-7.367			
NO	$\mu_Q$	-2.126	-2.471	0.659	0.033			
	$\mu_{\text{CNDO}}$	-0.401	-0.176	1.463	1.083	-1.31		
	$\mu_{\text{DIXON}}$	-1.197	-1.219					
NO	$\mu_{\text{SH}}$			0.768	0.586			
	$\mu_Q$	-1.507	-1.700	-0.516	-0.914			
	$\mu_{\text{CNDO}}$	-0.606	-0.474	0.124	-0.060	-0.64		
NO	$\mu_{\text{DIXON}}$	-1.302	-1.412					
	$\mu_{\text{SH}}$			0.510	-0.419			
	$\mu_Q$	-0.581	-0.651	0.453	0.329			
NO	$\mu_{\text{CNDO}}$	-0.288	-0.247	0.928	0.999	-0.15		
	$\mu_{\text{DIXON}}$	-0.432	-0.502					
	$\mu_{\text{SH}}$			3.652	3.313			
$\mu_{\text{experimental}}^b$								
FH	CH	BH	NH	OH	CN	BF	CO	NO
1.819	1.460	1.270	1.490	1.660	1.450	0.500	-0.112	0.159

<sup>a</sup> Pople and Beveridge (1970).

<sup>b</sup> Taken from Green (1975).

We conclude by noting that the CNDO results are improved with the MSO basis set and that this fact can mean that the MSO have the required properties of making the approximations involved in the CNDO method more plausible than they are for the STO. However, our results say little or nothing about the MSO as applied to molecular calculations in general.

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