Studies in Electronegativity. III. Comparison of Molecular Charge Distributions and Dipole Moments Calculated Using the OCEE and the CNDO/2 Schemes*

BJØRN VOIGT

Department of Physical Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

The Overlap Corrected Electronegativity Equalization (OCEE) theory outlined previously has been applied to the calculation of the dipole moments and charge distributions of HF, H₂O, NH₃, HCN, H₂CO, CH₄, and the four F-substituted methanes, and the results have been compared with those obtained using the CNDO/2 scheme. The two theories predict dipole moments of comparable accuracy, but they lead to charge distributions which are significantly different in some cases. These differences originate mainly because of the manner in which neutral penetration energy terms are treated in the respective schemes.

1. INTRODUCTION

In the initial publication in this series,¹ hereafter referred to as Paper I, a detailed theoretical analysis of the principle of electronegativity equalization was presented. The treatment was based upon the assumption that the electronic structure of the molecule under consideration could be adequately described by means of localized molecular orbitals. It was concluded from this analysis that the electronegativity equalization principle provides a theoretically sound foundation for MO calculations as long as certain molecular corrections to the electronegativities are taken into account. The Overlap Corrected Electronegativity Equalization (OCEE) scheme, proposed in Paper I, includes those corrections which arise from overlap dis-

tributions and from the penetration of atomic orbitals into the charge clouds of other atoms in the molecular environment. The latter correction comprises the, as it turns out, important effects of polarization of atoms.

The OCEE scheme has now been applied to the calculation of the dipole moments and charge distributions of a series of molecules in which delocalization effects are commonly regarded as being small. The results have been compared with those obtained using the CNDO/2 scheme of Pople, Santry and Segal²⁻⁴ which has been particularly successful in the calculation of dipole moments.⁵ Simultaneously the CNDO/2 scheme has been used to assess the importance of delocalization effects in these molecules. This has been achieved by estimating the accuracy with which the canonical CNDO/2—MO's could be localized.

Although the two theories appear rather different, especially with respect to their initial premises, they nevertheless have certain features in common. Both assume the validity of the Mulliken approximation,^{1,7} and both use Mulliken electronegativities as the key semi-empirical parameters. The methods differ, however, in that explicit penetration energy terms, which are neglected in the CNDO/2 scheme,⁸ are retained as significant corrections to the Mulliken electronegativities in the OCEE theory. Comparison of appropriate results obtained using the two schemes might therefore be expected in general to shed light on the importance of penetration effects, and in particular to

* Based in part on a thesis presented to the University of Copenhagen in partial fulfillment of the requirements for the lic. scient. degree.

demonstrate the degree to which these effects are accounted for implicitly by the CNDO/2 parameterization scheme.

2. OCEE THEORY

The basis of the OCEE theory is the assumption that the electronic ground state of a molecule can be approximated by a single Slater determinant constructed from N doubly occupied, localized molecular orbitals (LMO's) of the form

$$\psi_k = \frac{1}{\sqrt{2}} \left\{ (1 + \gamma_k) \phi_{k1} + (1 - \gamma_k) \phi_{k2} \right\} / \sqrt{1 + S_k + (1 - S_k) \gamma_k^2} \quad (1)$$

$$S_k \equiv \int \phi_{k1} \phi_{k2} d\mathbf{v}; k = 1, 2, \dots, N$$

The ϕ 's denote atomic hybrid orbitals (AHO's) which are assumed to be normalized and real. In cases where (1) describes a lone pair $\phi_{k1} = \phi_{k2} (= \psi_k)$.

Using a Taylor expansion in the bond polarity, γ_k , the charge distribution (a.u.) from two electrons occupying the LMO (1) is:

$$2\psi_k^2 = Q_{k1}\phi_{k1}^2 + Q_{k2}\phi_{k2}^2 + Q_{kS}\phi_{k1}\phi_{k2}/S_k \quad (2)$$

$$Q_{k1} = q_k \{ 1 + 2\gamma_k + 2S_k q_k \gamma_k^2 - 2(1 - S_k) q_k \gamma_k^3 \} + O(\gamma_k^4)$$

$$Q_{k2} = q_k \{ 1 - 2\gamma_k + 2S_k q_k \gamma_k^2 + 2(1 - S_k) q_k \gamma_k^3 \} + O(\gamma_k^4)$$

$$Q_{kS} = 2q_k S_k \{ 1 - 2q_k \gamma_k^2 \} + O(\gamma_k^4); q_k = (1 + S_k)^{-1}$$

The overlap change, Q_{kS} , assumes its maximum value in the homopolar case ($\gamma_k = 0$) and decreases as the bond becomes polar, regardless of the direction of polarity.

The requirement that the total energy be stationary (minimum) with respect to changes in the variational parameters, γ_k , can now be formulated as

$$-\frac{\partial E}{\partial \gamma_k} = \left(-\frac{\partial E}{\partial Q_{k1}} \right) \left(\frac{dQ_{k1}}{d\gamma_k} \right) + \left(-\frac{\partial E}{\partial Q_{k2}} \right) \left(\frac{dQ_{k2}}{d\gamma_k} \right) + \left(-\frac{\partial E}{\partial Q_{kS}} \right) \left(\frac{dQ_{kS}}{d\gamma_k} \right) =$$

$$X(k1) \frac{dQ_{k1}}{d\gamma_k} + X(k2) \frac{dQ_{k2}}{d\gamma_k} +$$

$$X(kS) \frac{dQ_{kS}}{d\gamma_k} = 0 \quad (3)$$

the generalized electronegativity, X , being defined as the derivative of the energy with respect to the signed charge. Note especially the presence in (3) of the overlap electronegativity, $X(kS)$. This term, which has a leading contribution linear in γ_k , cannot be interpreted in terms of electronegativity equalization of the two bonding orbitals. Instead it enters into the description of the inherent inertia of the bond to weaken as the overlap charge decreases.

The general equation (3) is written in more explicit form in Paper I. The energy expression used assumes that the LMO's are mutually orthogonal, *i.e.* that overlaps between non-bonded AHO's are neglected. This may be justified if the true basis set for the calculation is made up of orbitals which have been symmetrically orthogonalized on all AHO's except that with which a bond (if any) has been formed. Details concerning how this orthogonalization is performed are treated in Ref. 2, where a discussion of the relation between the proper basis sets of the OCEE and the CNDO schemes is presented.

Further simplification in (3) has been achieved using the Goeppert-Mayer and Sklar,⁸ the Mulliken,⁹ the Wolfsberg-Helmholz,¹⁰ and the Ruedenberg¹¹ approximations. The latter is a generalization of the Mulliken approximation applicable to $\phi_i(1)\phi_j(2)$.

In Paper I two possible operators to which the Wolfsberg-Helmholz approximation could be applied were discussed. The relation resulting from the choice of one of these (eqn. 45, Paper I) is unsatisfactory in that it effectively contains the exchange integral between the two bonded orbitals. This is not consistent with the fact that the two electrons in the bond have opposite spins. Also, it is highly inconvenient from the computational point of view.

Use of the alternative possibility completely avoids this problem. If the energy contributions up to and including terms of third order in the bond polarities are retained, eqn. (3) now takes the form (for details see Paper I):

$$2S_k q_k \gamma_k [X^0(k1) + X^0(k2)](G - 1) +$$

$$q_k \gamma_k [J(k1, k1) + J(k2, k2) - 2J(k1, k2)] +$$

$$\sum_{j \neq k}^N 2q_j A_{kj} \gamma_j =$$

$$[1 - 3(1 - S_k) q_k \gamma_k^2] [X^0(k1) - X^0(k2)] \quad (4)$$

G is a Wolfberg-Helmholz-type parameter and $A_{kj} = J(k1,j1) + J(k2,j2) - J(k1,j2) - J(k2,j1) - \frac{1}{2}[K(k1,j1) + K(k2,j2) - K(k1,j2) - K(k2,j1)]$

$J(i,j)$ represents the Coulomb interaction between ϕ_i and ϕ_j and $K(i,j)$ is the corresponding exchange interaction. The generalized homopolar electronegativity for ϕ_{k1} (centered on atom A) is defined by

$$X^0(k1) \equiv X_M(k1) + \sum_{C \neq A}^{\text{atoms}} PE_C(k1) + \frac{1}{2}[J(k1,k2) - K(k1,k2)] \quad (5)$$

where X_M denotes the Mulliken electronegativity and PE_C is the penetration energy of the orbital into the neutral atom C in the appropriate valence state. A similar definition applies to $X^0(k2)$. The three terms on the left-hand side of eqn. (4) are referred to as bond, diagonal inductive, and off-diagonal inductive terms, respectively.

2.1. Exchange interactions in the OCEE theory. The expressions for X_M and PE_C in (5) both contain exchange terms corresponding to undefined spins of the electrons in singly occupied AHO's. The presence of $K(k1,k2)$ is therefore only formal, as the term cancels with a similar term in the penetration energy into the atom on which ϕ_{k2} is centred.

Of the remaining exchange interactions, the two-center integrals have been shown to be negligible when calculated using the true basis set.² In the following we discard even the one-center contributions while attempting a rough correction for the consequent error *via* the parameterization of the one-center Coulomb integrals (Section 3.4).

Because of the effective neglect of exchange, application of the rather dubious Ruedenberg approximation in practice becomes somewhat redundant, having only marginal influence on the computations. From the formal point of view, however, the approximation is expedient being the only one which will produce the correct exchange contributions to the Mulliken electronegativity.

3. OCEE CALCULATIONS

The OCEE calculations, details of which are given in the present section, were based upon

eqns. (4) and (2). The system of eqns. (4) was solved for the bond polarities by iteration. Each step involved solution of a set of n linear equations, n being the number of non-equivalent bonds in the molecule. The dipole moment with proper inclusion of overlap moments was evaluated from the charge distributions (2). This expression was also used to calculate atomic charges, overlap charges being divided equally between the AHO's involved. The charges to be used in the comparison with the CNDO scheme have been discussed previously.²

3.1. Basis set and hybridization. The set of basis functions used to construct the hybrids of the OCEE scheme is identical to that employed in the CNDO/2 scheme, *i.e.* a Slater-type orbital basis with orbital exponents chosen using the Slater-Zener rules, except that the value 1.2 was adopted for hydrogen.

The hybridization schemes were such that σ -bonding AHO's were always directed along the internuclear axis. This condition, combined with the appropriate symmetry, was sufficient to determine the form of the bonding orbitals for most of the atoms in the molecules considered. Uncertainties remained only for C and N in HCN, for O in H_2CO and for F in general. The hybridization of C in HCN was assumed to be perfectly diagonal, and three calculations were performed for each of the HCN and H_2CO molecules with different σ -bonding orbitals for the hetero-atoms in each case. The s -character of the bonding AHO on F (*i.e.* the square of the coefficient of the $2s$ -orbital) was determined by a least squares fit of the calculated to the corresponding observed dipole moments for the fluoromethanes.

3.2. Effective electronegativities. The main orbital property governing the signs and magnitudes of the bond polarities is the generalized homopolar electronegativity X^0 . The primary contributor to this is the well-known Mulliken electronegativity of the orbital in the appropriate valence state of the atom. But important molecular PE-corrections are also present. The last term in the definition (5) is required in order to avoid self-interaction of the electron. A term of this nature occurs in the penetration energy into the atom with which the bond is formed.

The Mulliken electronegativity of an AHO depends rather strongly upon the form of the

hybrid. Values were obtained from the tables of Hinze and Jaffé¹² using linear interpolation based upon the orbital *s*-character. Penetration energies were calculated neglecting exchange contributions between non-bonded orbitals.²

The very important electronegativity difference appearing on the right-hand side of eqn. (4) contains only the difference in Mulliken electronegativity (ΔX_M) and the difference in total penetration energy (ΔPE). It has been customary in semi-empirical calculations to assume that penetration energies are approximately the same for all atomic orbitals, so that terms similar to the ΔPE -term have usually been neglected (Section 4.1). The present calculations indicate that the validity of this assumption may be questionable.

3.3. Penetration energies. The ΔPE -term proved to be very significant indeed. Its sign was always opposite to that of the ΔX_M -term, and its numerical value in some cases exceeded 50 % of the corresponding ΔX_M .

It is not surprising that ΔX_M and ΔPE have opposite signs since orbitals characterized by low Mulliken electronegativities have small orbital exponents (great penetrating ability) and *vice versa*. The relatively large magnitude of ΔPE , especially when atoms of very different electronegativities are involved, originates mainly from the fact that large electronegativities occur only for atoms with more than half-filled valence shells, *i.e.* for atoms carrying lone pairs. The atomic charge distributions in the relevant valence states of these atoms will, in general, possess a dipole moment which is directed so as to give rise to large positive contributions to the penetration energies of orbitals on neighbouring atoms. This is illustrated by the results obtained for HF, which is an extreme case because of its large ΔX_M and short bond length. With an *s*-character for the bonding F-orbital of 0.28, ΔX_M amounts to 10.4 eV. The ΔPE -term is calculated to -4.8 eV, 75 % of which arises from the polarization of the F-atom.

Penetration energies into non-polarized atoms such as H and C decrease exponentially with distance and are relatively small even for orbitals centred on neighbouring atoms but forming bonds to others. The PE-terms for polarized atoms remain important for larger distances because of the monopole-dipole-type interac-

tions involved. The effects of this for the fluoromethanes will be discussed in Section 5.2.

3.4. Two-electron integrals. Neutral penetration energies are probably reasonably well represented in calculations such as those presented here, because correlation effects are similar in attraction and repulsion. However, this is unlikely to be so for the inductive terms in (4). It is true that, even in this case, any one orbital interacts with an overall neutral charge distribution, *i.e.* with the charge displacement within a bond, but the effective distances to the positive and negative parts may differ substantially. The value of the Coulomb integral between the bonded orbitals which enters the bond term might also be expected to be strongly influenced by correlation.

To take account of such correlation effects parameterization has been invoked for all two-electron integrals not entering the penetration energy terms. For one-orbital integrals the Pariser formula:¹³

$$J(i,i) \cong I_V(i) - A_V(i)$$

has been used. Values for the valence state ionization potentials and electron affinities were obtained from the tables of Hinze and Jaffé.¹² The remaining integrals, including one-center two-orbital integrals, were parameterized using the method of Mataga and Nishimoto;¹⁴ that is:

$$J(i,j) \cong e^2/(r + a_{ij}), \quad a_{ij} \cong 2e^2/[J(i,i) + J(j,j)]$$

To include effects of hybridization, the distances *r* were those between the centers of gravity of the charge distributions involved.

The use of the centers of gravity can be justified for non-overlapping charge distributions. Thus significant errors are limited to one-center integrals and to the integral involving the two bonded orbitals. This latter integral will be somewhat overestimated, but since it occurs twice, with opposite sign, in the diagonal coefficient in (4) the effect of this error will be reduced. This diagonal coefficient also contains the purely empirical Wolfberg-Helmholz parameter, through which further corrections may be achieved. The one-center two-orbital integrals, on the other hand, will probably be underestimated in the above parameterization scheme. Although its extent may not be adequate, this effect will provide the desired correction for

the neglect of the corresponding one-center exchange interactions (Section 2.1).

3.5. The Wolfsberg-Helmholz parameters G basically expresses the ratio of the overlap electronegativity to the mean of the electronegativities of the bonded orbitals.¹ By performing a calculation for H_2O in which the resulting dipole moment is constrained to be approximately the observed value, a G of 1.9 was obtained. This is similar to those used in earlier applications of the Wolfsberg-Helmholz approximation, in most of which values between 1.5 and 2.0 have been employed.

4. CNDO/2 CALCULATIONS

The CNDO/2 scheme is a semi-empirical approximation of the LCAO-SCF theory the basis of which is the complete neglect of differential overlap (CNDO) between atomic orbitals. The basic theory, notation, and parameterization are described in detail in the original publications by Pople *et al.*^{3-5,15}

4.1. Neutral penetration energy terms occur in the diagonal element of the Fock operator in the CNDO theory. However, these terms only account for the spherical average (around the center in question) of the penetration of the orbital into other atoms for which charge distributions have been spherically averaged about their respective centers.⁷ Furthermore, in CNDO/2 the nuclear attraction integral V_{AB} is approximated by $-Z_B\gamma_{AB}$ ⁵ *i.e.* explicit penetration terms are altogether absent in this scheme.

Contrary to what appears to be the case for the CNDO/2 scheme, the OCEE scheme would be seriously unbalanced without PE-corrections (Section 3.3). It should be noted, however, that it is the polarization part of these terms which makes them of such importance in the latter theory. This part cannot be included explicitly in any CNDO scheme. One of the purposes of the present comparison has therefore been to investigate how well these polarization effects are accounted for implicitly by the CNDO/2 parameterization. Before this can be described in a satisfactory way, however, it is necessary to examine some difficulties which arise in making the comparison itself.

4.2. CNDO localization procedure. To make comparison of the OCEE and the CNDO/2

schemes meaningful, the localized description assumed in the former must be reasonably adequate for the molecules treated. This point was investigated by means of the CNDO/2 scheme. Localization of the occupied canonical CNDO/2-MO's was achieved by applying the unitary transformation which maximizes the sum of one-orbital Coulomb integrals over the MO's (computed within the CNDO approximation). This localization criterion was originally proposed by Lennard-Jones and Pople¹⁶ and its extension to the CNDO scheme has been studied by Trindle and Sinanoglu.¹⁷

The Self Energy Localized (SEL) MO's so constructed have large contributions from orbitals on two atoms, at the most, and are easily recognized as representing bonds and lone pairs in the molecule. All bonds and σ -type (hybridized) lone pairs could be well localized, the secondary contributions (*i.e.* the coefficients for AO's on distant centers) being relatively small (< 0.05). The π -type lone pairs, however, are delocalized to larger extents in some cases. This is discussed in the following section.

Since delocalization effects are unimportant in those SELMO's which involve hybridization, it is possible to formulate approximate hybridization schemes for the various atoms from the CNDO/2 calculation. This has been done by neglecting secondary contributions, rescaling the primary coefficients to fulfil the normalization condition and analyzing the resulting localized MO's in terms of normalized AHO's. The directions of the bonding AHO's lie in all cases within a few degrees of those of the appropriate internuclear axes. The effective orbitals s -characters are listed in column 6 of the tables.

A necessary requirement for perfect localization is that all hybridization transformations obtained in this way be unitary. Hence ideally the sum of the s -characters of the AHO's on an atom should equal 1. This condition was fulfilled (to within the accuracy of the calculation) for all atoms carrying lone pairs. Lone pair s -characters have therefore been omitted from the tables. The deviation from unity for carbon may be taken as a rough measure of the degree of delocalization.

4.3. Delocalization effects in CNDO/2. By far the dominant delocalization effect in the CNDO/2 results is that of π -type lone pair

Table 1.

Molecule ^a	Dipole moments (D) Obs.	OCEE	CNDO/2	CNDO/2D ^b	Orbital s-character OCEE	Charges (e) OCEE	OCEE ^d	CNDO/2	CNDO/2D ^b
H ₂ O	1.846 ^f	1.86 ^e	2.15	1.76	O .200	H +.124	H +.103	H +.143	H +.196
NH ₃	1.468 ^g	1.70	2.09	1.50	N .227	H +.059	H +.046	H +.078	H +.127
		2.34			N .333	H +.095	H +.065		
					C _N .500	N _π -.049	N _π -.046		
					C _H .500	N _σ +.028	N _σ +.017	H +.070	H +.100
HCN	2.986 ^h	2.64	2.42	2.15	N .500	H +.095	H +.065	N -.092	N -.160
					C _N .500	N _π -.032	N _π -.031	N _π -.093	N _π -.097
					C _H .500	N _σ -.021	N _σ -.012	N _σ +.001	N _σ -.063
					N .667	H +.094	H +.064	C +.022	C +.060
		2.76			C _N .500	N _π -.043	N _π -.041		
					C _H .500	N _σ -.060	N _σ -.032		
					O .333	H +.062	H +.046		
		2.85			C _O .382	O _π -.191	O _π -.186		
					C _H .309	O _σ -.035	O _σ -.025	H -.017	H +.011
H ₂ CO	2.339 ⁱ	3.11	1.89	1.63	O .500	H +.062	H +.046	O -.184	O -.255
					C _O .382	O _π -.160	O _π -.156	O _π -.167	O _π -.171
					C _H .309	O _σ -.113	O _σ -.078	O _σ -.100	O _σ -.165
					O .667	H +.060	H +.044	O _π +.083	O _π +.081
		3.24			C _O .382	O _π -.169	O _π -.164	C +.218	C +.233
					C _H .309	O _σ -.146	O _σ -.099		

^a Geometries from Ref. 23. ^b From Ref. 19. ^c See Section 4.2. for method of calculation. ^d See Ref. 2. ^e Used in determination of the Wolsberg-Helmholz parameter (Section 3.4). ^f Birnbaum, G. and Chatterjee, S. K. *J. Appl. Phys.* 23 (1952) 220. ^g Coles, D. K., Good, W. E., Bragg, J. K. and Sharbaugh, A. H. *Phys. Rev.* 82 (1951) 877. ^h Battacharya, B. N. and Gordy, W. *Phys. Rev.* 119 (1960) 144. ⁱ Shooley, J. N. and Sharbaugh, A. H. *Phys. Rev.* 82 (1951) 95.

delocalization onto carbon and hydrogen atoms. This type of back donation, or reverse hyperconjugation, has been noted earlier in methanol by Pople and Segal.⁴ It may be thought of as arising from the interaction of the antisymmetrical CH_n orbital with a completely filled π -system (the lone pair).

For the molecules treated in this work, reverse hyperconjugation was especially important in formaldehyde. In this case the oxygen $2p$ lone pair in the molecular plane (O_π) donates 0.083 of an electron to the CH_2 group. One third of this is transferred to the hydrogens. The mechanism leads to a lowering of the dipole moment by 0.57 D.

Back donation from lone pairs is also found in the fluoromethanes. However, although more lone pairs take part in the delocalization, less charge is transferred because of the increased bond distances and stronger binding of the lone pair electrons. The F_π -charge given in column 9 of Table 2 is the total charge acquired by the atom *via* reverse hyperconjugation. The effect of these charge displacements on the dipole moments is about the same in the three unsymmetrical molecules (0.29, 0.41, and 0.43 D, respectively, for mono-, di-, and trifluoromethane).

If it is assumed (a) that the excess in the sum of s -characters for C in CH_3F is caused entirely by the mixing of CH – LMO's and F lone pairs, and (b) that the effect on the s -character of any C-orbital is proportional to the amount of charge donated by the lone pairs, then the s -characters for various C-hybrids found in the remaining fluoro-methanes may be rationalized. Using assumption (a) the basis s -characters are 0.200 for C-orbitals bound to F and $(1 - 0.200)/3 = 0.267$ for orbitals forming bonds to H. Correcting these values for the increasing number of F-atoms and, according to (b), for the increase in the charge donated by each of these, the apparent s -characters become 0.233, 0.274, and 0.341 for the C_F -orbitals in CH_2F_2 , CHF_3 , and CF_4 , respectively, and 0.333 and 0.378 for the C_H -orbitals. These numbers all agree closely with the corresponding numbers in column 6 of Table 2, so it seems reasonable to assert that the C-hybrids taking part in the σ -bonding are essentially unchanged through this series of fluoromethanes, the changes derived from the CNDO/2 results largely being due to the approximate nature of the method of derivation.

5. RESULTS AND DISCUSSION

The computations were made using an IBM-7094 at the Northern Europe University Computing Center (NEUCC), Lundtofte, Denmark, and a GIER at the H. C. Ørsted Institute, University of Copenhagen. Penetration energies in the OCEE scheme were computed using a FORTRAN IV version of the DIATOM program.²⁰ The remainder of the OCEE scheme calculations were programmed in GIER-ALGOL. The CNDO/2 calculations were performed using a FORTRAN IV program derived from that written by Segal.²¹ The results are presented in Tables 1 and 2. When available,¹⁹ the CNDO/2D dipole moments and charges, obtained using the symmetrically orthogonalized atomic basis,¹⁸ have been included in the tables.

5.1. Dipole moments and hybridization. The OCEE method is capable of predicting dipole moments with an overall accuracy comparable to that of the CNDO/2 scheme.

Formaldehyde is the only molecule for which the OCEE value for the dipole moment is both poor and simultaneously greatly at variance with the values computed using the CNDO/2 wavefunction. This is undoubtedly due to the failure of the OCEE theory to take into account the back donation of charge from the O_π lone pair. The resulting reduction of the dipole moment in CNDO/2 (Section 4.3) is nearly the same as the difference between the OCEE prediction and the observed value.

The effect of lone pair delocalizations in the fluoro-methanes is apparently well provided for by the use of the hybridization of F as a parameter.

It may appear surprising that the OCEE procedure leads to a higher s -character (and thereby greater electronegativity) for the bonding F-orbital than that given by the CNDO calculation. It should be noted therefore, that the CNDO scheme is likely to underestimate the hybridization of polarizable atoms since it ignores polarization contributions to the interactions between atoms.²²

The underestimation of polarization in CNDO/2 ought to be particularly significant for HF because of the short bond distance. This furnishes an explanation for the large discrepancy between the F hybridization schemes in the two calculations. Note, however, that there is no *a priori* justification for the direct transfer, adopted in the OCEE calculation, of F-hybridization from the fluoromethanes to HF.

Table 2.

Molecule ^a	Dipole moments (D) Obs.	Dipole moments (D) OCEE		Orbital s-character OCEE		Charges (e) OCEE		OCEE ^a	CNDO/2	CNDO/2D ^a
		OCEE	CNDO/2	OCEE	CNDO/2 ^a	OCEE	CNDO/2 ^a			
CH ₄	0	0	0	C .250	C .261	H -.000 C +.001	H +.012 C -.048	H -.000 C +.001	H +.012 C -.048	—
CH ₃ F	1.855 ^c	1.78 ^b	1.72	C _F .235 C _H .255 F .28	C _F .200 C _H .295 F .203	H +.029 F -.162 C +.075	H +.005 F -.194 (F _π +.040) C +.180	H +.021 F -.141 C +.078	H +.005 F -.194 (F _π +.040) C +.180	H +.036 F -.240 C +.132
CH ₃ F ₂	1.96 ^d	2.02 ^b	1.95	C _F .236 C _H .264 F .28	C _F .229 C _H .333 F .215	H +.056 F -.126 C +.140	H -.006 F -.194 (F _π +.047) C +.400	H +.041 F -.108 C +.134	H -.006 F -.194 (F _π +.047) C +.400	—
CHF ₃	1.645 ^e	1.68 ^b	1.66	C _F .245 C _H .265 F .28	C _F .271 C _H .373 F .228	H +.080 F -.089 C +.187	H -.018 F -.199 (F _π +.053) C +.615	H +.058 F -.076 C +.170	H -.018 F -.199 (F _π +.053) C +.615	—
CF ₄	0	0	0	C .250 F .28	C .320 F .232	F -.062 C +.248	F -.202 (F _π +.067) C +.808	F -.053 C +.212	F -.202 (F _π +.067) C +.808	—
HF	1.8195 ^f	1.89	1.85	F .28	F .178	H +.187	H +.232	H +.160	H +.232	H +.298

^a See corresponding footnotes to Table 1. ^b Used in determination of the hybridization scheme of F. ^c Larkin, M. and Gordy, W. *J. Chem. Phys.* 38 (1963) 2329. ^d Lide, D. R. *J. Amer. Chem. Soc.* 74 (1952) 3548. ^e Shoolery, J. N. and Sharbaugh, A. H. *Phys. Rev.* 82 (1951) 95. ^f Weiss, R. *Phys. Rev.* 131 (1963) 659.

According to the arguments above it would be expected that the *s*-characters in CNDO/2 of the bonding orbitals of N and O in HCN and H₂CO would be too low. In these cases the OCEE results give no indications since the computed dipole moments are remarkably insensitive to the hybridization schemes of the hetero-atoms. This is due partly to the balancing of differences in electronegativity and in penetration energy of the orbitals involved, and partly to the large induction between components of multiple bonds.

5.2. Charge distributions. The net atomic charges are listed in columns 7–10 of Tables 1 and 2. The values to be compared are the ones marked OCEE' and CNDO/2 since these were obtained using very similar basis sets.² However, comparison of the original OCEE and the CNDO/2D charges also leads to the same conclusions. Such a comparison is justifiable because of the insignificance of the non-bonded overlaps.

Charges calculated for electronegative atoms are generally less negative in OCEE' than in CNDO/2. Further carbon atoms and hydrogen atoms directly bound to centers of high electronegativity are less positive, and atoms separated by two bonds from an electronegative atom are more positive.

These differences originate mainly from the respective ways in which penetration energies are treated in the two schemes. The difference in generalized homopolar electronegativity, which is the driving force in the transfer of charge, is greatly reduced by the penetration contributions included in the OCEE theory (Section 3.3). Consequently, the polarities of the most polar bonds are lower than the corresponding values obtained from the CNDO/2 scheme. This effect accounts for the lower negative charges on N, O, and F in OCEE. It also accounts for the larger electron density on the hydrogen atoms bound to these atoms, and for some of the differences on the carbon charges. The electronegativities of orbitals forming bonds in the vicinity of polarized atoms (CH- and CF-bonds here) contain significant non-bonded penetration terms. These act in favour of the occupancy of the orbital closest to the center of polarization and lead to a further increase in electron density on the carbon atoms in the molecules considered.

In view of the important role played by the neutral penetration energy terms in the OCEE theory, it is at first sight surprising that corresponding results from the two calculations only deviate extensively for relative few of the molecules. The main reason for this, however, is that the over-estimation of differences in effective electronegativity in the CNDO/2 scheme is counter-balanced by the use of large two-electron repulsion integrals which prevent large charges developing on any atom.

The results for methane and its four F-substituted analogs demonstrate clearly how the two theories account for charge displacements. The two calculations give similar values for the CF-polarity in CH₃F. Non-bonded penetration terms for this bond are insignificant. The result indicates the ability of the CNDO/2 parametrization to simulate the effect of bonded penetration. Going through the series, non-bonded penetration (polarization) becomes increasingly important in the OCEE treatment. This, together with the increasing competition for electrons between the fluorines, brings about an appreciable decrease in the amount of charge transferred through the CF-bond. The results of the CNDO/2 calculation show a weak *increase* in the polarity of this bond.

In Section 2 it was pointed out that polarity of a bond reduces the bonding since it decreases the overlap charge in the bond. Consequently the bond length should decrease with decreasing polarity, reaching a minimum for the homopolar case. This feature is well illustrated by the CF-bonds in the fluoromethanes. The CF-distances observed for mono- to tetrafluoromethanes²³ (1.385, 1.358, 1.332, and 1.323 Å, respectively) correlate well with the polarities obtained from the OCEE calculation. The comparison may be made quantitative if bond distance is expressed as a linear function of the square of polarity [see eqn. (2)] or, equivalently, as a linear function of bond order. After a least squares fit of the two constants the corresponding calculated CF-distances are 1.3854, 1.3566, 1.3339, and 1.3221 Å. All values are well within the uncertainty limits of the observed bond length. Extending these results, a homopolar paraffinic CF-bond should have a length of about 1.31 Å.

It should be noticed that a correlation of the above type also appears in the CNDO/2 results, in which the *F_π*-charges may be taken as

measures of the double bond character of the CF-bond. However, their increase along the series seems too weak to account for the observed bond shortening. This is supported by explicit CNDO/2 calculations of geometries from energy minima for the fluoro-methanes.^{18a}

The charge alternation noted by Pople and Gordon^{6,15} in CNDO/2 results for F-substituted hydrocarbons, and illustrated by the increase in electron density on the hydrogen atoms along the series of fluoro-methanes, is mainly due to reverse hyperconjugation. Each of the hydrogens in mono-, di, and trifluoromethane receive charges of -0.005 , -0.011 , and -0.018 , respectively, through delocalization of fluorine lone pairs. This back donation of charge is no doubt a genuine effect, but when the effect of polarization of atoms is properly included the latter will dominate the picture as suggested by the OCEE results.

The fluoromethanes have recently been the subjects of two accurate *ab initio* calculations performed at the Hartree-Fock level.^{25,26} Both calculations yield strongly positive hydrogens ($+0.3$ and $+0.2$) and negative fluorines (-0.3). Except for one case the charges on these atoms vary in the same directions and by comparable amounts as those found in the OCEE calculation. The carbon charges, on the other hand, undergo dramatic changes along the series (from -1 in CH_4 to $+1$ in CF_4). It is probable that the hydrogens are calculated to be too positive. As recognized²⁵ it is "not very sensible to suppose" that the hydrogens in CH_4 each carry a charge of $+0.3$. This particular result may be due to the use of diffuse orbitals. These make the charges derived from a Mulliken population analysis rather formal quantities which do not reflect the actual electron densities at the atoms. There may also be more fundamental inadequacies in the method of calculation. That this is at least partly the case may be seen from the computed dipole moments which are consistently 30–40 % too large.

6. CONCLUSIONS

The OCEE and the CNDO/2 schemes both appear wellbalanced in the sense that molecular dipole moments may be calculated with fair accuracy. However, the charge distributions

obtained with the two theories may in certain cases be rather different.

The OCEE theory emphasizes the neutral penetration energy contributions to the effective electronegativities, thereby achieving substantial equalization of the latter. These penetration terms appear particularly important when polarized atoms are present. The effective dipole moment of the charge distributions around these atoms contributes significantly to the field around other atoms in the molecule. Inclusion of these effects in the OCEE scheme is made possible through the use of a localized description. This limits the applicability of the theory to a particular, not very well-defined, class of molecules. Furthermore, the hybridization schemes used will always be questionable, even when chosen according to principles more fundamental than those upon which the present work was based.

The CNDO/2 scheme is more general in that it can be applied to any molecular system, and it gives no problems in choice of hybridization. But in making the various approximations all effects arising from the polarization of atoms are lost. This appears in some cases to have serious consequences upon the calculated charge distributions. The success of CNDO/2 theory in predicting dipole moments is largely due to the counter-balancing of overestimated differences in effective electronegativity by the effects of the use of large two-electron repulsion integrals. When these parameters are evaluated according to semi-empirical arguments charge displacements, and therefore dipole moments tend to become too large.²⁴

The INDO (Intermediate Neglect of Differential Overlap) scheme,^{27,15} which differs from the CNDO scheme in the inclusion of one-center exchange integrals, also describes the interaction between atoms in terms of spherical charge distributions. With calculated two-electron integrals this scheme produces dipole moments and charge distributions similar to those given by the CNDO/2 scheme.¹⁵ When parameterization is introduced the computed dipole moments again become too large.^{28,29} Spherical averaging is not used in the NDDO (Neglect of Diatomic Differential Overlap) scheme,^{3,15,30} and all polarization effects are retained in this scheme. But for the calculation of dipole moments and charge distributions it

appears somewhat superfluous to include *all* two-electron integrals involving two one-center charge distributions.

It has recently been demonstrated²² that it is possible to construct an approximate LCAO-SCF scheme which, while retaining the necessary invariance properties, is intermediate between the INDO- and the NDDO-schemes. This has been named DRINDO (Dipoles Retained . . .) and incorporates the main effects of polarization of atoms in the selfconsistent field. In view of the conclusions drawn from the present comparison there is hope that some parameterized version of the DRINDO-scheme will produce more accurate dipole moments than does the INDO-scheme whilst simultaneously retaining the facility of the latter to predict other molecular properties. Work in progress is directed towards this end.

REFERENCES

1. Voigt, B. and Dahl, J. P. *Acta Chem. Scand.* **26** (1972) 2923.
2. Voigt, B. *Acta Chem. Scand. A* **28** (1974) 1043.
3. Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys.* **43** (1965) S 129.
4. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* **43** (1965) S 136.
5. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* **44** (1966) 3289.
6. Pople, J. A. and Gordon, M. J. *Amer. Chem. Soc.* **89** (1967) 4253.
7. Dahl, J. P. *Acta Chem. Scand.* **21** (1967) 1244.
8. Goeppert-Mayer, M. and Sklar, A. L. *J. Chem. Phys.* **6** (1938) 645.
9. Mulliken, R. S. *J. Chim. Phys.* **46** (1949) 497; 675.
10. Wolfsberg, M. and Helmholz, L. *J. Chem. Phys.* **20** (1952) 837.
11. Ruedenberg, K. *J. Chem. Phys.* **19** (1951) 1433.
12. Hinze, J. and Jaffé, H. H. *J. Amer. Chem. Soc.* **84** (1962) 540.
13. Pariser, R. *J. Chem. Phys.* **21** (1953) 568.
14. Mataga, N. and Nishimoto, K. *J. Phys. Chem.* **13** (1954) 140.
15. Pople, J. A. and Beveridge, D. L. *Approximate Molecular Orbital Theory*, McGraw-Hill, New York 1970, (a) Table 4.7.
16. Lennard-Jones, J. E. and Pople, J. A. *Proc. Roy. Soc. (London) A* **202** (1950) 446; **A 210** (1951) 190.
17. Trindle, C. and Sinanoglu, O. *J. Chem. Phys.* **49** (1968) 65; *J. Amer. Chem. Soc.* **91** (1969) 853.
18. Löwdin, P. O. *Sv. Kem. Tidskr.* **67** (1955) 380.
19. Shillady, D. D., Billingsley, F. P. and Bloor, J. E. *Theoret. Chim. Acta* **21** (1971) 1.
20. Switendick, A. C. and Corbato, F. J. *Diatomic molecular Integral Program*, Program 29, Quantum Chemistry Program Exchange, Indiana University.
21. Segal, G. A. *CNDO/2 Program*, Program 91, Quantum Chemistry Program Exchange, Indiana University.
22. Voigt, B. *Theoret. Chim. Acta* **31** (1973) 289.
23. Sutton, L. E., Ed., *Tables of Interatomic Distances*, The Chemical Society, London 1958 and 1965.
24. Sichel, J. M. and Whitehead, M. A. *Theoret. Chim. Acta* **11** (1968) 220, 254.
25. Schwartz, M. E., Coulson, C. A. and Allen, L. C. *J. Amer. Chem. Soc.* **92** (1970) 447.
26. Brundle, C. R., Robin, M. B. and Basch, R. *J. Chem. Phys.* **53** (1970) 2196.
27. Pople, J. A., Beveridge, D. L. and Dobosh, P. A. *J. Chem. Phys.* **47** (1967) 158.
28. Baird, N. C., Dewar, M. S. J. and Sustmann, R. *J. Chem. Phys.* **50** (1969) 1275.
29. Shanshal, M. *Theoret. Chim. Acta* **21** (1971) 149.
30. Murrell, J. N. and Harget, A. J. *Semi-empirical SCF MO Theory of Molecules*, Wiley, London 1972.

Received June 4, 1974.