

**373.** *Localised Molecular Orbitals in the Self-consistent Field Wave Functions of Linear Molecules. Part II.\* Atomic Charges and Dipole Moments.*

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The localised molecular orbitals of some self-consistent field wave functions reported in the preceding paper are analysed in terms of the populations and charges on the atoms in the molecule. The population-analysis procedure is recast in a simple form to deal with localised molecular orbitals.

The  $\sigma$ , but not the  $\pi$ , atomic charges follow the usual electronegativity ideas closely. The dipole moments obtained from the atomic charges are not alone a useful guide to molecular dipole moments. The sum of these and the hybridisation, or atomic, dipoles gives a better guide to the observed dipole moment.

DURING the last few years, there has been published<sup>1</sup> a number of detailed self-consistent field wave functions for some di-, tri-, and tetra-atomic linear molecules. These molecules are, from a chemist's point of view, quite small, but many of the general problems of valence theory arise in them and the results should be of wider value. The wave functions are calculated by means of the Hartree-Fock approximation and the important assumptions made in using such wave functions concern the validity of the molecular-orbital method in general and of the one-determinant approximation to the wave function in particular. A further approximation is involved in the use of Slater atomic orbitals as basis functions. The best wave functions of this general type now available are built on basis functions which are more flexible than Slater atomic orbitals, but their interpretation<sup>2</sup> raises many problems beyond those considered here. In calculations of this kind, no empirical results are incorporated at any stage and it is this feature which distinguishes them from the familiar semiempirical methods. At the same time, it must be emphasised that these techniques are still in their early stages and the results may undergo substantial revision in due course.

These wave functions may be used directly in the computation of various observables, but this is not the only objective for the chemist who also wants insight into the factors governing the formation and properties of the molecule. Such common and useful ideas as the two-electron bond, the lone pair, the atom in the molecule and its charge, and the general idea of hybridisation are not immediately apparent in wave functions of this kind. In the preceding paper, it was shown that the two-electron bond and the lone pair can be discerned in these wave functions and, at the same time, the hybridisations in the various hybrid atomic orbitals were written out and shown to fall into a simple pattern. In the present paper, the charge on the atom in the molecule and its connection with the molecular dipole moment are explored.

The localisation procedure showed that a lone pair is characterised by one hybridisation parameter and that a two-electron bond is characterised by two hybridisation parameters and one polarity parameter. These are the numerical raw material, or primary parameters, which come directly from the wave function. From these, other secondary parameters can be obtained which are more closely related to observables of the molecule. An example of a secondary parameter is the charge,  $Q$ , on the atom in the molecule; this is often thought to be connected with the observed dipole moment. The first task is to examine how these secondary parameters are derived from the hybridisation and polarity parameters.

\* Part I, preceding paper.

<sup>1</sup> Ref. 7 of preceding paper.

<sup>2</sup> Mulliken, *J. Chem. Phys.*, 1962, **36**, 3428.

Previous attempts to extract from molecular-orbital wave functions such quantities as the atomic charges led by several steps<sup>3</sup> to Mulliken's population-analysis methods.<sup>4</sup> One of the end products of this analysis is the electron population of an atom, divided usually into  $\sigma$  and  $\pi$  populations. By comparing these results with the structure of the free atom it is possible to see, to some extent, how the atom is modified when it is incorporated into the molecule. There is some arbitrariness in the method, but the numbers which emerge seem to be sensible and helpful.

There are some difficulties when existing population-analysis methods are applied to delocalised molecular orbitals. For example, it is not always possible to separate clearly the effects of different electron pairs in the molecules. If we think of the six-electron  $\sigma$  frame of the nitrogen and the carbon monoxide molecule, the original method does not allow one to separate clearly and to examine the three electron pairs which, in a first approximation, make up the  $\sigma$  bond and the two lone pairs. Nor is it possible to see how the hybrid atomic orbitals and the total hybridisations are connected with the promotion of the atom in the molecule. There arise also questions about the definitions of the populations and charges on the atom in the molecule. These and some other difficulties can now be resolved by carrying out a population analysis of the localised molecular orbitals reported in the preceding paper. A much more detailed picture of the factors which govern molecular structure and properties then begins to emerge.

The basic technique of the conversion of delocalised into localised molecular orbitals has been dealt with in Part I. The next task is to reformulate the population-analysis procedure in terms of localised molecular orbitals.

*Population Analysis of Localised Molecular-orbital Wave Functions.—(a) Introduction.* Population analysis is, in the main, an attempt to understand molecular wave functions in terms of electron-density functions. The quantum mechanical nature of the problem, which is recognised in the original computations, is thus suppressed in the interpretation of the results. To do this, we write the complete  $2n$ -electron Hartree-Fock wave function ( $\Psi$ ) of a closed-shell ground state in terms of localised molecular orbitals as

$$\Psi = |\cdots \lambda_i(a)\bar{\lambda}_i(a) \cdots \mu_j(ab)\bar{\mu}_j(ab) \cdots|. \quad (1)$$

In this equation, a bar denotes a  $\beta$  spin, the absence of a bar an  $\alpha$  spin. A lone pair on atom  $a$  is denoted by  $\lambda_i(a)$  and a molecular orbital of a two-electron bond between atom  $a$  and  $b$  is denoted by  $\mu_j(ab)$ . The  $1s$  atomic orbitals and any  $\pi$ -electron molecular orbitals are omitted throughout. We use  $i, j \cdots$  to label lone pairs and two-electron-bond molecular orbitals,  $a, b \cdots$  to label atoms, and  $r, s \cdots$  to label atomic orbitals. The simple spin-free electron-density function in real space is then given by

$$\rho = 2n \int \Psi^* \Psi d\tau_2 \cdots d\tau_{2n} d\sigma_1 \quad (2)$$

where  $\sigma$  is the spin variable and  $d\tau = dx dy dz d\sigma$ . Expansion gives

$$\rho = \{ \cdots 2[\lambda_i(a)]^2 \cdots 2[\mu_j(ab)]^2 \cdots \}; \quad (3)$$

so the electron-density function appears as a sum of terms each of which is associated with a lone pair or a two-electron-bond molecular orbital.

Some reservations are necessary when using equation (3). It is only exact if all the molecular orbitals are exactly orthogonal, but it is not in general possible to have all the molecular orbitals both completely localised and exactly orthogonal unless atomic orbitals of high principal quantum number are used in the wave function. Further, there is a great deal of arbitrariness in equation (3). It could be replaced by an equation involving only the atomic orbitals of a single atom if a single-centre expansion were used either in the wave function or in the electron-density function. For practical purposes, however, such

<sup>3</sup> Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413.

<sup>4</sup> Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338, 2343.

wave functions, *i.e.*, those for atomic orbitals of high principal quantum number, are of little help in visualising the situation; so it is natural to confine the terms in the wave function to atomic orbitals of low principal quantum number, and this removes much of the arbitrary character from equation (3).

(b) *Lone pairs.* A lone pair is now written as

$$\lambda_i(\mathbf{a}) = h_i(\mathbf{a})2s_a + \{1 - [h_i(\mathbf{a})]^2\}^{1/2}2p\sigma_a. \quad (4)$$

The notation is that used in the preceding paper and is adequate for hybridisation involving only the  $2s$  and  $2p\sigma$  atomic orbitals. The electron-density function of an electron in a lone pair is then

$$\rho_i(\mathbf{a}) = [h_i(\mathbf{a})]^2(2s_a)^2 + \{1 - [h_i(\mathbf{a})]^2\}(2p\sigma_a)^2 + 2h_i(\mathbf{a})\{1 - [h_i(\mathbf{a})]^2\}^{1/2}(2s_a)(2p\sigma_a), \quad (5)$$

which, on integration, gives

$$1 = [h_i(\mathbf{a})]^2 + \{1 - [h_i(\mathbf{a})]^2\}. \quad (6)$$

The two-electron population of the lone pair is then divided into a fraction  $2[h_i(\mathbf{a})]^2$  in the  $2s$  atomic orbital and a fraction  $2\{1 - [h_i(\mathbf{a})]^2\}$  in the  $2p\sigma$  atomic orbital. These populations may be written in a useful notation as

$$l(i; \mathbf{a}) = 2; \quad l(i; \mathbf{a}_{2s}) = 2[h_i(\mathbf{a})]^2; \quad l(i; \mathbf{a}_{2p\sigma}) = 2\{1 - [h_i(\mathbf{a})]^2\}. \quad (7)$$

The third term on the right of equation (5) vanishes on integration but is not itself everywhere zero. This term cannot be represented by a point charge, so it is necessary to neglect it for the present.

(c) *Molecular orbitals of the two-electron bond.* These may be written

$$\mu_j(\mathbf{ab}) = p_j(\mathbf{a})h_j(\mathbf{a}) + p_j(\mathbf{b})h_j(\mathbf{b}), \quad (8)$$

and the derived electron-density function is

$$\rho_j(\mathbf{ab}) = [p_j(\mathbf{a})]^2[h_j(\mathbf{a})]^2 + [p_j(\mathbf{b})]^2[h_j(\mathbf{b})]^2 + 2p_j(\mathbf{a})p_j(\mathbf{b}).S[S^{-1}h_j(\mathbf{a})h_j(\mathbf{b})], \quad (9)$$

where  $S$  is the overlap integral,  $\int h_j(\mathbf{a})h_j(\mathbf{b})dxdydz$ . Integration gives

$$1 = [p_j(\mathbf{a})]^2 + [p_j(\mathbf{b})]^2 + 2p_j(\mathbf{a})p_j(\mathbf{b}).S. \quad (10)$$

The third term on the right of equation (10) is the overlap population and it belongs to both atoms. If we then insist that the two electrons in the molecular orbital be assigned to atoms only, this overlap population must be divided between the two atoms in some way. In the homonuclear case, the overlap population must be divided equally between the two atoms, but, in the general case, an arbitrary decision must be made. There are two simple possibilities. The first is Mulliken's original decision to divide the overlap population equally in all cases. Then the population of the hybrid atomic orbital of atom  $a$  is given by

$$l(j; \mathbf{a}) = [p_j(\mathbf{a})]^2 + p_j(\mathbf{a})p_j(\mathbf{b}).S, \quad (11)$$

and this may then be subdivided into the population of the  $2s$  atomic orbital,  $l(j; \mathbf{a}_{2s})$ , and that of the  $2p\sigma$  atomic orbital,  $l(j; \mathbf{a}_{2p\sigma})$ , by the equations

$$l(j; \mathbf{a}_{2s}) = [h_j(\mathbf{a})]^2l(j; \mathbf{a}); \quad l(j; \mathbf{a}_{2p\sigma}) = \{1 - [h_j(\mathbf{a})]^2\}l(j; \mathbf{a}). \quad (12)$$

The second possibility is to divide the overlap population in the proportions  $[p_j(\mathbf{a})]^2$  and  $[p_j(\mathbf{b})]^2$ , which is equivalent simply to renormalising these quantities so that their sum is unity. A prime will be used throughout to distinguish material based on this division of the overlap population. As an example, the population of the hybrid atomic orbital on atom  $a$ ,  $l'(j; \mathbf{a})$ , is given by

$$l'(j; \mathbf{a}) = [p_j(\mathbf{a})]^2\{[p_j(\mathbf{a})]^2 + [p_j(\mathbf{b})]^2\}^{-1}, \quad (13)$$

and this may be subdivided as before into the populations of the 2s and the  $2p\sigma$  atomic orbitals.

The charges in the hybrid atomic orbitals,  $q(j; a)$ , are defined as the difference between the populations of the hybrid atomic orbital in the molecule and those of the neutral free atom suitably hybridised. For a lone pair, this charge is always zero and for the hybrid atomic orbital of a two-electron-bond molecular orbital it is given by

$$q(j; a) = 1 - l(j; a). \quad (14)$$

Defined in this way, the charge has a negative sign if charge accumulates in the hybrid atomic orbital in the molecule as compared with the free atom.

It is now a simple matter to define the total populations of the 2s and  $2p\sigma$  atomic orbitals of the atom in the molecule by the equations

$$L(a_{2s}) = \sum_j l(j; a_{2s}) + \sum_i l(i; a_{2s})$$

and

$$L(a_{2p\sigma}) = \sum_j l(j; a_{2p\sigma}) + \sum_i l(i; a_{2p\sigma}). \quad (15)$$

In these equations, the first summation is over the hybrid atomic orbitals of the two-electron-bond molecular orbitals, and the second is over the lone pairs of the atom. The total atom population is given by

$$L(a) = L(a_{2s}) + L(a_{2p\sigma}). \quad (16)$$

Terms for the 1s atomic orbitals and any  $\pi$  molecular orbitals may be added if required. If we denote by a script letter the analogous terms for the free atom, then the various atomic charges may be defined by

$$Q(a_{2s}) = \mathcal{L}(a_{2s}) - L(a_{2s}),$$

$$Q(a_{2p\sigma}) = \mathcal{L}(a_{2p\sigma}) - L(a_{2p\sigma}),$$

and

$$Q(a) = \mathcal{L}(a) - L(a)$$

As before, an accumulation of charge in the atomic orbital, or on the atom, in the molecule leads to negative signs for these charges. If primed quantities are used in the original definitions, primes must be attached to the  $Q$  and  $L$ .

*Results.*—The  $\sigma$  atomic charges for the equal and the unequal division of the overlap population are reported in Figs. 1 and 2, respectively. The  $\pi$  charges, calculated in the usual way,<sup>4</sup> are reported in Fig. 3. The total calculated dipole moment,  $\mu_T$ , and the various contributions to this from the atomic charges,  $\mu_q$  from the lone pairs,

Li+0.31	-0.31H			B+0.12	-0.12H
C 0.00	0.00H			N-0.08	+0.08H
O-0.13	+0.13H			F-0.15	+0.15H
		C+0.35	-0.35O		
O-0.13	+0.13C	O	S+0.43	-0.43C+0.22	-0.22O
C+0.09	-0.09C	C	N+0.26	-0.26N	N
O+0.16	-0.16N	O	H+0.26	-0.26C+0.14	-0.14N
	H	C	C-0.21	+0.21H	
	N	C	C+0.12	-0.12N	
	C	C	C+0.06	-0.06C	

FIG. 1.  $\sigma$  Atomic charge ( $q_\sigma$ ) for equal division of the overlap population.

Li+0.50	-0.50H			B+0.17	-0.17H
C 0.00	0.00H			N-0.09	+0.09H
O-0.15	+0.15H			F-0.18	+0.18H
		C+0.46	-0.46O		
O-0.16	+0.16C	O	S+0.56	-0.56C+0.28	-0.28O
C+0.12	-0.12C	C	N+0.32	-0.32N	N
O+0.19	-0.19N	O	H+0.43	-0.43C+0.20	-0.20N
	H	C	C-0.36	+0.36H	
	N	C	C+0.17	-0.17N	
	C	C	C+0.07	-0.07C	

FIG. 2.  $\sigma$  Atomic charge ( $q_{\sigma}$ ) for unequal division of the overlap population.

			-0.25	+0.25		
			C	O		
-0.08	+0.16	-0.08	-0.33	+0.20	+0.12	
O	C	O	S	C	O	
+0.11	-0.22	+0.11	+0.26	-0.52	+0.26	
C	C	C	N	N	N	
+0.08	-0.16	+0.08		-0.06	+0.06	
O	N	O	H	C	N	
	N	C	-0.10	+0.10		
			C	N		
	C	C	-0.04	+0.04		
			C	C		

FIG. 3.  $\pi$  Atomic charges ( $q_{\pi}$ ).

$\mu_L$ , and from the hybrid atomic orbitals of the two electrons bonds,  $\mu_B$ , are shown in the Table.

Molecule	Dipole moments (in D).*									
	$\mu_G$	$\mu_G'$	$\mu_L$		$\mu_B$		$\mu_{\pi}$	$\mu_{exp}$		
LiH .....	+2.45	+3.83	—		+3.64	+6.09	+5.8 ‡			
BH .....	+0.71	+1.01	-2.80		-1.17	-3.29				
CH .....	0.0	0.0	-1.58		-1.27	-2.85				
NH .....	-0.40	-0.45	-0.99		-1.18	-3.02				
OH .....	-0.60	-0.70	-0.71		-1.01	-2.86				
FH .....	-0.66	-0.79	-0.55		-0.86	-2.07	-1.80 §			
			C	O	C	O				
CO † (A) ...	+0.54	—	-3.26	+2.13	+0.09	-0.79	-1.29	0.11 ¶		
(B) ...	+0.54	—	-3.31	+1.67	+0.53	-0.03	-0.60			
			N	C(N)	C(H)	N(C)				
HCN .....	+1.77		+2.07	+1.98	-3.05	+0.07	+2.84	3.00 **		
			O	S	C(S)	C(O)	S(C)	O(C)		
OCS .....	-1.31		-1.30	+2.81	+3.25	-1.80	+0.84	-0.79	+1.70	0.72 ††

\* A plus sign denotes a dipole with its positive pole to the left of the molecules as written in column 1. Column heading symbols are explained in the paragraph immediately preceding the discussion. The subheadings under  $\mu_L$  and  $\mu_G$  for CO, HCN, and COS specify the atom of the lone pair or hybrid atomic orbital. Symbols such as C(H) denote a hybrid atomic orbital on carbon directed towards hydrogen. † There are two alternative localisation routes for carbon monoxide. These are labelled (A) and (B), as in Part I. ‡ Wharton, Gold, and Klemperer, *J. Chem. Phys.*, 1960, **33**, 1255. § Magnuson and Weiss, quoted by Nesbet, *J. Chem. Phys.*, 1962, **36**, 1527. ¶ Burrus, *J. Chem. Phys.*, 1959, **31**, 1270. \*\* Ghosh, Tranbarulo, and Gordy, *J. Chem. Phys.*, 1953, **21**, 308. †† Dakin, Good, and Coles, *Phys. Rev.*, 1946, **70**, 560.

## DISCUSSION

The present results support some, but not all, of the common ideas about atomic charges. It is convenient to discuss first  $\sigma$  and  $\pi$  atomic charges separately, then the relation between them, and finally the connection between atomic charges and dipole moments.

$\sigma$  Atomic Charges.—The first point is that it does not matter very much at the present time which of the two divisions of the overlap populations is used in defining the atomic charges. The charges ( $q$ ) resulting from equal division of the overlap population are somewhat ( $\sim 25\%$ ) smaller than those ( $q'$ ) resulting from unequal division but, since the atomic charge is not directly observable, this difference in absolute values is not very important. The important features are the relative sizes of the atomic charges in a series of molecules.

The diatomic hydrides are the simplest molecules of this set because they contain no  $\pi$  bonds. Along the series lithium hydride to hydrogen fluoride, the amount of charge shifts increasingly from hydrogen to the other element. The point of equal atomic charge is at carbon. This is a sensible result because the electronegativity increases to the right along the series of first-row elements. There is no complication from changing hybridisation in the hybrid atomic orbital of the first-row element since hybridisation is constant in this series (cf. Part 1). In Fig. 4, the Pauling electronegativity numbers<sup>5</sup> are plotted

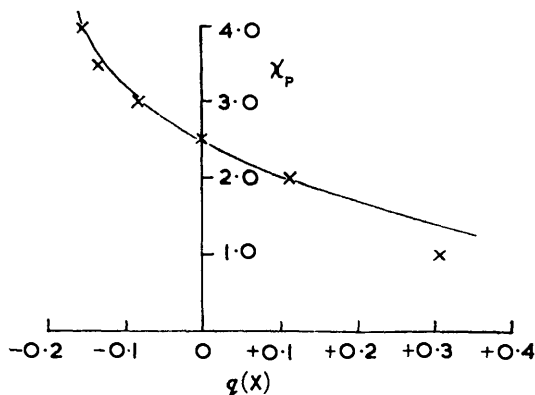


FIG. 4. Plot of Pauling's electronegativity numbers,  $\chi_P$ , against charge,  $q(X)$ , on X in HX.

against the charges on the first-row elements and a smooth curve is obtained, apart from the point for lithium. If the calculated charge on lithium in lithium hydride is correct, to fit the curve lithium must have a higher electronegativity number ( $\sim 1.5$ ) than the Pauling number (1.0). The "abnormal" result in the figure contrasts with the earlier result (Part 1) that lithium in lithium hydride uses a hybrid atomic orbital which contains 34% of the less electronegative  $2p\sigma$  atomic orbital, yet the hybrid as a whole is more electronegative than the almost pure  $2s$  atomic orbital which lithium uses in the lithium molecule. It appears then that care is required in using electronegativity arguments to deal with the easily promoted atoms to the left of the Periodic Table. On the whole, however, the atomic charges calculated for the diatomic hydrides are satisfactory.

The remaining molecules all contain  $\pi$  bonds. In thinking about such molecules, one should always consider the sum of the  $\sigma$  and the  $\pi$  effects and their mutual interaction or mutual polarisation. In the interests of simplicity, however, it is common practice to try to understand them separately and to suppose that the  $\sigma$  and the  $\pi$  charges separately will show regularities along a series of molecules. Figs. 1 and 3 show that the  $\sigma$  atomic charges behave much more regularly and in accordance with general expectation than do

<sup>5</sup> Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 3rd edn., 1960, p. 93.

the  $\pi$  atomic charges. This leads one to try to interpret the  $\sigma$  atomic charges alone in the first place, ignoring polarisation of the  $\sigma$  electrons by the  $\pi$  electrons. Then the  $\pi$  electron charges may subsequently be considered as the result of the sum of the electronegativity of the atom and its  $\sigma$  atomic charge. This is reasonable since the  $\pi$  electrons are indeed more polarisable than the  $\sigma$  electrons and so more responsive to electronegativity and atomic-charge effects.

The  $\sigma$  charges are intelligible on the basis of two assumptions about the electronegativities of the atoms and the hybrid atomic orbitals, namely, that (a) electronegativity increases to the right along the first-row elements; and (b) increasing the amount of the  $2s$  atomic orbital in a hybrid increases the hybrid's electronegativity. Both assumptions are conventional.<sup>5,6</sup>

Examples of assumption (a) include the diatomic hydride series discussed above, the polarity of carbon-oxygen bonds in carbon monoxide, carbon dioxide, and carbon oxysulphide, and the polarity of the carbon-nitrogen bonds in hydrogen cyanide and cyanogen. In fact, this feature is so familiar as not to require much exemplification. There are also several examples of the less familiar rule (b). A series of carbon-hydrogen bonds is the first of these. In the CH radical, carbon uses an approximately pure  $2p\sigma$  atomic orbital to form the bond. In hydrogen cyanide and in acetylene, carbon uses an approximately  $sp$  hybrid atomic orbital. The  $sp$  hybrid is more electronegative than the  $2p\sigma$  atomic orbital, so there should be more charge transferred to carbon in hydrogen cyanide and in acetylene than in the CH radical. This is the case, and the size of the effect is about 0.2 electron. A second example is the carbon-oxygen bond in carbon monoxide, carbon dioxide, and carbon oxysulphide. In carbon monoxide, carbon uses an approximately pure  $2p\sigma$  atomic orbital, while in carbon dioxide and carbon oxysulphide it uses an approximately  $sp$  hybrid atomic orbital. Accordingly, the charge transfer to oxygen is greater, by 0.1–0.2 electron, in carbon monoxide than in the other two molecules. A third example is  $C_3$ , where the end carbon atoms use approximately pure  $2p\sigma$  atomic orbitals in forming their  $\sigma$  bonds while the central carbon atom uses an approximately  $sp$  hybrid. As a result, there is charge transfer from the end atoms to the centre atom. The size of the effect here is about 0.1 electron.

Related but more complicated examples are  $N_3^-$  and  $NO_2^+$ . In these molecules, the  $\pi$  electron situation is not simple, but effect (b) may still operate because there is charge transfer from the end to the centre atom. In  $NO_2^+$ , the effect of feature (b) will be opposed by the electronegativity difference between oxygen and nitrogen, while in  $N_3^-$ , feature (b) will be enhanced by the formal positive charge on the centre nitrogen atom. The only example which seems to contradict (b) is  $C_4$ , but the results for this molecule are suspect (cf. Part I). On the whole, it seems that assumption (b) invokes a real effect.

A more subtle question is which of effects (a) and (b) is the more powerful when in opposition. The answer is that in no case is the hybridisation effect (b) sufficiently powerful to override the gross nature of the atom (a). The hybridisation effect is to be considered as a modification, not a contradiction, of the gross electronegativity of the atom. Examples are the carbon-nitrogen bond of hydrogen cyanide and cyanogen and the carbon-oxygen bond of carbon monoxide, carbon dioxide, and carbon oxysulphide.

It seems, then, that these  $\sigma$  charges can be understood on qualitative electronegativity arguments. The charges do not seem to be simply related to Hinze and Jaffe's calculated electronegativity numbers<sup>7</sup> which require, for example, that the carbon atom in hydrogen cyanide and in cyanogen is more electronegative than the nitrogen atom. It may be possible to reconcile the two sets of results by a more detailed use of the calculated hybridisations reported in Part I, but since these are probably approximate no such attempt has been made at this stage.

It is possible to discern in these results a little evidence that  $\sigma$  bonds polarise each other.

<sup>5</sup> Walsh, *Discuss. Faraday Soc.*, 1947, **2**, 18.

Hinze and Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

The carbon-hydrogen bond in hydrogen cyanide is more polar than that in acetylene, presumably because the polar carbon-nitrogen bond makes the carbon atom more electro-negative. In carbon oxysulphide, the carbon-oxygen bond is more polar than the same bond of carbon dioxide because the sulphur atom releases electrons to carbon in the former molecule, making it less electronegative. These are the only two reasonably clear instances of the effect in this set of molecules and too much emphasis should not as yet be put on the point.

$\pi$  Atomic Charges.—These charges (Fig. 3) do not agree with simple electronegativity numbers. The least complex of the  $\pi$  electron molecules are carbon monoxide and hydrogen cyanide, where there is no question of delocalised  $\pi$  bonds. Here then the electronegativity, the coulomb integral of  $\pi$  electron theory, and the atomic charges are single-valued functions of each other. In both carbon monoxide and hydrogen cyanide, the  $\pi$  electrons accumulate on carbon rather than on oxygen or nitrogen. The only simple explanation is that the  $\sigma$  electron accumulates on nitrogen or oxygen to an extent sufficient to reverse the apparent electronegativity of the atoms towards the  $\pi$  electrons. There are some complications for carbon monoxide, but the case of hydrogen cyanide is straightforward; and, if we neglect conjugation, cyanogen gives the same result as hydrogen cyanide.

The triatomic molecules would normally be considered as delocalised  $\pi$  electron systems. Simple  $\pi$  electron theory, with all coulomb integrals assumed equal, predicts  $\pi$  charges of zero at all atoms in the molecules carbon dioxide, carbon oxysulphide,  $N_3^-$ , and  $NO_2^+$ . The present results show that the oxygen atoms of carbon dioxide are slightly negative in the  $\pi$  electron frame, so the  $\sigma$ -electron accumulation on oxygen is not sufficient to reverse completely the electronegativity of oxygen with respect to carbon. In carbon oxysulphide, oxygen is positive in the  $\pi$  electron frame, and sulphur atom negative. This seems to be the result of a reversal of the usual electronegativity of both oxygen and sulphur by their surplus and deficit respectively, of  $\sigma$  electrons. The  $N_3^-$  and  $NO_2^+$  cases are ambiguous because of the formal charges.

In summary, it seems, from these results, that the effective electronegativity which an atom displays towards  $\pi$  electrons depends strongly on its  $\sigma$ -electron distribution. This is not in accord with conventional  $\pi$ -electron theory, which requires that atoms display their usual or gross electronegativity towards  $\pi$  electrons. It is necessary to re-emphasise at this point that the computations on which the present conclusions are based are far from definitive, but it is clear that, until these computations are confirmed or refuted, little reliance can be placed on the  $\pi$ -electron charges for large molecules calculated by semi-empirical or intuitive procedures. It seems likely that these semiempirically calculated charges are in some way representing the total charge on the atom in the molecule and not the  $\pi$  charge alone. This explains why the numbers obtained in this way are so useful in understanding experimental results, yet bear no relation to the  $\pi$  charges calculated in the present, much better, approximation. As an example concerning a large molecule, consider the nitrogen atom in pyridine. No doubt this atom will accumulate electrons in the molecule, and conventional  $\pi$  electron theory requires that it accumulates  $\pi$  electrons, but it is now clear that the electron accumulation may well occur in the  $\sigma$  frame and not in the  $\pi$  frame.

Atomic Charges and Dipole Moments.—It would be very convenient if a molecular dipole moment could be simply equated with the moment from the atomic charges ( $\mu_q$  or  $\mu_{q'}$ ). The dipole moments for the polar molecules of this set have been evaluated on this assumption, by using first the equal and then the unequal division of the overlap population in defining the atomic charges ( $q$  and  $q'$ ). The results are shown in the second and third columns of the Table. In three of the five cases, the calculated numbers are approximately half the observed dipole moment.

In principle, the hybridisation, or atomic, dipole <sup>8</sup> must also contribute to the molecular

<sup>8</sup> Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433; "Valence," Oxford University Press, 1952, p. 207.



dipole moment. This further dipole arises because the centroid of charge in a hybrid atomic orbital is not at the nucleus of the atom, whereas it has been assumed that an electron in a hybrid atomic orbital is "on" the atom. For some purposes, the latter may be the best view because it allows the radius of the atom to vary with its hybridisations. For dipole moments, however, it is clearly necessary to take account of these hybridisation dipoles. They occur both in the hybrid atomic orbitals of the two-electron bonds and in the lone pairs, and, individually, they are of the same order of magnitude as the atomic-charge dipoles. They are set out in detail in the Table so that their individual contributions to the total moment can be seen. It seems that the calculated total dipole moment is now in rather better agreement with experiment than when the atomic charge dipoles were used alone. The failure to find the small dipole moment of carbon monoxide is disappointing, but when the dependence of  $\mu_L$  and  $\mu_B$  on the localisation routes (A, B) is examined, it is clear that an uncertainty of  $\pm 0.5$  D is inevitable. It is fair to conclude that such results give an indication whether the experimental dipole moment will be small ( $< 1$  D), medium (1–3 D), or large ( $> 3$  D), but that closer agreement between experiment and theory may be fortuitous.

This work was begun while the author was at the Laboratory of Molecular Spectra and Structure, University of Chicago, and was supported by the Office of Naval Research, U.S.A. The author is indebted to Professor R. S. Mulliken for many discussions on these and other points.

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[Received, June 19th, 1962.]

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