764. *Localised Molecular Orbitals in Self-consistent Field Wave Functions. Part III.*[1] *Hybridisations, Atomic Charges, and Dipole Moments in Non-linear Molecules.*

By David Peters.

The localisation technique applied earlier to the self-consistent field wave functions of some linear molecules is now extended to the wave functions of the non-linear molecules water, ammonia, and formaldehyde. The results are very similar to those for the linear molecules. The lone pairs are close to pure atomic orbitals, except for that of ammonia which seems to be heavily hybridised. The hybrid atomic orbitals of the two-electron bonds are close to $2p\sigma$-atomic orbitals, except for those of the carbon atom of formaldehyde, which are heavily hybridised. The σ-atomic charges agree, on the whole, with expectations from the usual electronegativity ideas but the π-electron charges of formaldehyde do not. The atomic charges, unlike the hybridisations, are not sensitive to the detailed form of the wave function. A breakdown of the total calculated dipole moment into contributions from atomic charges and from hybridisation dipoles is given. As in the linear molecules, the hybridisation dipoles are large, particularly those of the lone pairs, and there is nothing to suggest that the atomic charges alone are a useful guide to the observed dipole moment.

During the last few years, a number of detailed wave functions have been computed[2] for some small but chemically interesting molecules which are built from two, three, or four atoms of the first row of the Periodic Table. Most of these are linear molecules, but a few wave functions for non-linear molecules have also been reported; these were

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[1] Peters, *J.*, 1963, 2003, 2015 (Parts I and II, respectively, of the series).

[2] Cf. ref. 7 of Part I.

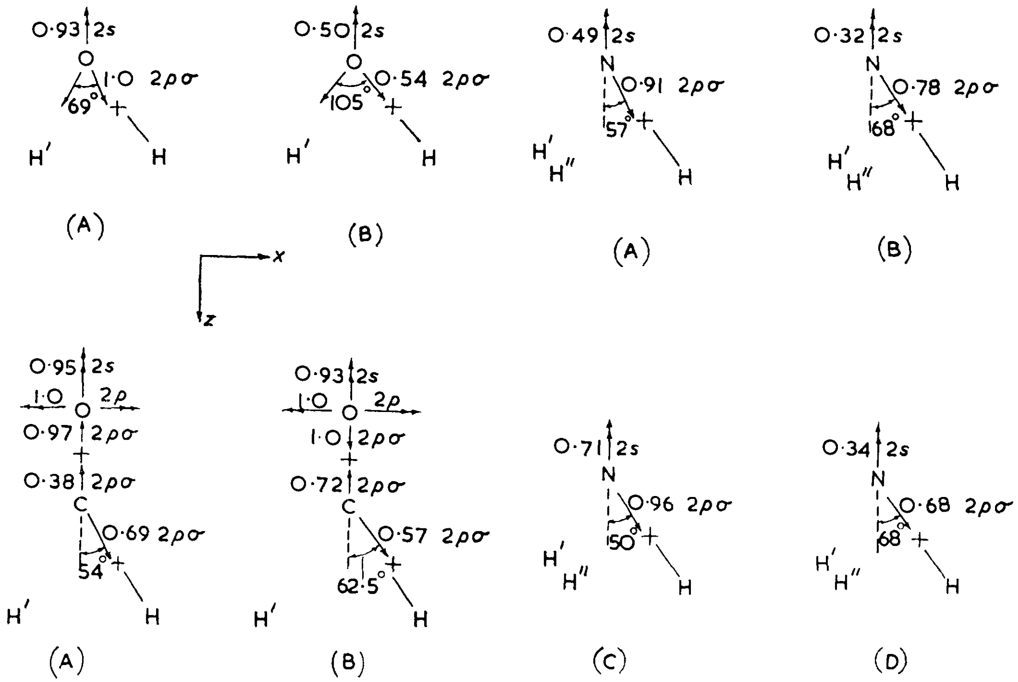

FIG. 1. Hybridisations in the lone pairs and two-electron bonds of the water, ammonia, and formaldehyde molecules. (Cf., footnote to Table 1 and the footnotes to the Figures in Part I of this series for detailed explanation of the notation.)

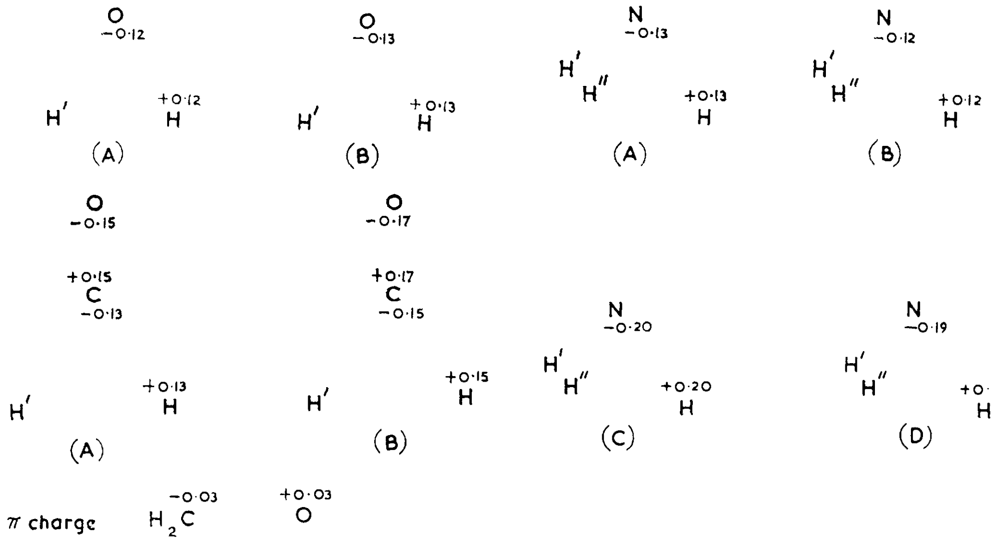

FIG. 2. Atomic charges in the water, ammonia, and formaldehyde molecules. (A negative sign for the atomic charge shows that the population of the hybrid atomic orbital is greater than one.)

TABLE I.

Localised molecular orbitals in the water, ammonia, and formaldehyde molecules.

Water.

There are two possible localisation routes, (A) and (B).

(A) $$\mathrm{BMO} = 0{\cdot}5630(1s_{\mathrm{H}}) + 0{\cdot}6630\,\{-0{\cdot}0094(2s_{\mathrm{O}}) + 0{\cdot}9996\,[0{\cdot}8254(2pz_{\mathrm{O}}) + 0{\cdot}5645(2px_{\mathrm{O}})]\} - 0{\cdot}1985(1s_{\mathrm{H'}})$$

$$\mathrm{LP} = 0{\cdot}9629(2s_{\mathrm{O}}) - 0{\cdot}2720(2pz_{\mathrm{O}})$$

The localisation requirement is that the lone pair be free from $1s_{\mathrm{H}}$ and $1s_{\mathrm{H}}'$. These orbitals were reported by Ellison and Schull.[3]

(B) $$\mathrm{BMO} = 0{\cdot}5002(1s_{\mathrm{H}}) + 0{\cdot}6195\,\{0{\cdot}6763(2s_{\mathrm{O}}) + 0{\cdot}7366\,[0{\cdot}6086(2pz_{\mathrm{O}}) + 0{\cdot}7934(2px_{\mathrm{O}})]\} - 0{\cdot}2457(1s_{\mathrm{H'}})$$

$$\mathrm{LP} = 0{\cdot}7053(2s_{\mathrm{O}}) - 0{\cdot}7034(2pz_{\mathrm{O}}) - 0{\cdot}1765(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$$

The localisation requirement is that the hybrid atomic orbitals on oxygen point along the internuclear lines.

Ammonia.

There are two possible localisation routes for the Slater atomic-orbital wave functions [(A), (B)] and two for the Hartree–Fock atomic-orbital wave functions [(C), (D)].

(A) $$\mathrm{BMO} = 0{\cdot}5098(1s_{\mathrm{H}}) + 0{\cdot}6263\,\{0{\cdot}3073(2s_{\mathrm{N}}) + 0{\cdot}9516\,[0{\cdot}5380(2pz_{\mathrm{N}}) + 0{\cdot}8429(2px_{\mathrm{N}})]\} - 0{\cdot}0823(1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

$$\mathrm{LP} = 0{\cdot}6991(2s_{\mathrm{N}}) - 0{\cdot}7151(2pz_{\mathrm{N}})$$

The localisation requirement is that the lone pair be free from $1s_{\mathrm{H}}$, $1s_{\mathrm{H'}}$, and $1s_{\mathrm{H''}}$. These localised orbitals were reported by Duncan.[4]

(B) $$\mathrm{BMO} = 0{\cdot}5025(1s_{\mathrm{H}}) + 0{\cdot}6102\,\{0{\cdot}4709(2s_{\mathrm{N}}) + 0{\cdot}8826\,[0{\cdot}3754(2pz_{\mathrm{N}}) + 0{\cdot}9268(2px_{\mathrm{N}})]\} - 0{\cdot}0866(1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

$$\mathrm{LP} = 0{\cdot}5704(2s_{\mathrm{N}}) - 0{\cdot}8213(2pz_{\mathrm{N}}) - 0{\cdot}0549(1s_{\mathrm{H}} + 1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

The localisation requirement is that the hybrid atomic orbitals on nitrogen point along the internuclear lines.

(C) $$\mathrm{BMO} = 0{\cdot}4799(1s_{\mathrm{H}}) + 0{\cdot}6564\,\{0{\cdot}2096(2s_{\mathrm{N}}) + 0{\cdot}9778\,[0{\cdot}6425(2pz_{\mathrm{N}}) + 0{\cdot}7662(2px_{\mathrm{N}})]\} - 0{\cdot}1018(1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

$$\mathrm{LP} = 0{\cdot}8434(2s_{\mathrm{N}}) - 0{\cdot}5371(2pz_{\mathrm{N}})$$

The localisation requirement is that the lone pair be free from $1s_{\mathrm{H}}$, $1s_{\mathrm{H'}}$, and $1s_{\mathrm{H''}}$.

(D) $$\mathrm{BMO} = 0{\cdot}4574(1s_{\mathrm{H}}) + 0{\cdot}6293\,\{0{\cdot}5626(2s_{\mathrm{N}}) + 0{\cdot}8268\,[0{\cdot}3754(2pz_{\mathrm{N}}) + 0{\cdot}9268(2px_{\mathrm{N}})]\} - 0{\cdot}1155(1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

$$\mathrm{LP} = 0{\cdot}5810(2s_{\mathrm{N}}) - 0{\cdot}8139(2pz_{\mathrm{N}}) - 0{\cdot}0859(1s_{\mathrm{H}} + 1s_{\mathrm{H'}} + 1s_{\mathrm{H''}})$$

The localisation requirement is that the hybrid atomic orbitals on nitrogen point along the internuclear line.

Formaldehyde.

There are many possible localisation routes for this molecule. The best two which have been found are (A) and (B).

(A) $$\mathrm{BMO(CO)} = 0{\cdot}5578\,[0{\cdot}7902(2s_{\mathrm{C}}) - 0{\cdot}6129(2pz_{\mathrm{C}})] + 0{\cdot}6786\,[-0{\cdot}1715(2s_{\mathrm{O}}) + 0{\cdot}9852(2pz_{\mathrm{O}})]$$

$$\mathrm{BMO(CH)} = 0{\cdot}4790(1s_{\mathrm{H}}) + 0{\cdot}6010\,\{0{\cdot}5561(2s_{\mathrm{C}}) + 0{\cdot}8311\,[0{\cdot}5940(2pz_{\mathrm{C}}) + 0{\cdot}8045(2px_{\mathrm{C}})]\} - 0{\cdot}0214(2s_{\mathrm{O}}) - 0{\cdot}1327(2pz_{\mathrm{O}}) - 0{\cdot}0724(1s_{\mathrm{H'}})$$

$$\mathrm{LP(O)} = 1{\cdot}000(2px_{\mathrm{O}}) - 0{\cdot}1887(1s_{\mathrm{H}} - 1s_{\mathrm{H'}}) + 0{\cdot}0692(2px_{\mathrm{C}})$$

$$\mathrm{LP(O)} = 0{\cdot}9750(2s_{\mathrm{O}}) - 0{\cdot}2205(2pz_{\mathrm{O}}) + 0{\cdot}0154(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$$

The localisation requirements are that BMO(CH) be free from $2px_{\mathrm{O}}$, that the second LP(O) be free from $2s_{\mathrm{C}}$ and $2pz_{\mathrm{C}}$, and that BMO(CO) be free from $1s_{\mathrm{H}}$ and $1s_{\mathrm{H'}}$.

(B) $$\mathrm{BMO(CO)} = 0{\cdot}5299\,[0{\cdot}5328(2s_{\mathrm{C}}) - 0{\cdot}8463(2pz_{\mathrm{C}})] + 0{\cdot}6704\,[-0{\cdot}0160(2s_{\mathrm{O}}) + 0{\cdot}9999(2pz_{\mathrm{O}})]$$

$$\mathrm{BMO(CH)} = 0{\cdot}4675(1s_{\mathrm{H}}) + 0{\cdot}6055\,\{0{\cdot}6593(2s_{\mathrm{C}}) + 0{\cdot}7519\,[0{\cdot}4630(2pz_{\mathrm{C}}) + 0{\cdot}8864(2px_{\mathrm{C}})]\} - 0{\cdot}0860(1s_{\mathrm{H'}})$$

$$\mathrm{LP(O)} = 1{\cdot}000(2px_{\mathrm{O}}) - 0{\cdot}1887(1s_{\mathrm{H}} - 1s_{\mathrm{H'}}) + 0{\cdot}0692(2px_{\mathrm{C}})$$

$$\mathrm{LP(O)} = 0{\cdot}9637(2s_{\mathrm{O}}) - 0{\cdot}2669(2pz_{\mathrm{O}}) - 0{\cdot}0094(1s_{\mathrm{H}} + 1s_{\mathrm{H'}}) - 0{\cdot}0866(2s_{\mathrm{C}})$$

The localisation requirements are that BMO(CH) be free from $2s_{\mathrm{O}}$, $2px_{\mathrm{O}}$, and $2pz_{\mathrm{O}}$, that the BMO(CO) be free from $1s_{\mathrm{H}}$ and $1s_{\mathrm{H'}}$, and that the second LP(O) be free from $2pz_{\mathrm{C}}$.

The axis system used in this Table is that shown in Fig. 1 with the molecules oriented as shown in that Figure. In ammonia, the unprimed hydrogen atom is in the *xz*-plane. BMO = bonding molecular orbital, LP = lone pair. The hybrid atomic orbitals are written in normalised form. The LP's and BMO's are written so that they are normalised *after* deletion of the imperfections in the localisation.

calculated in the self-consistent field molecular-orbital scheme, whose goal is the restricted (based on atomic orbitals) Hartree–Fock wave function of the molecule. This procedure uses the general apparatus of molecular-orbital theory and, in particular, the one-determinant approximation to the wave function. The value of these wave functions in chemical thinking is often not realised since they are reported in an unfamiliar form, and it is part of the purpose of this series of papers to set out these results in a more familiar language and to show how far they agree with the usual chemical thought on valency theory. Some details are lost in the translation, but it is pleasing to find that many of the usual ideas of chemistry are now supported by numerical evidence. The linear molecules were dealt with in the earlier work [1] and this is now extended to the non-linear molecules.

A thorough discussion of the localisation procedure used in this work was given in the earlier papers and a brief summary will be enough here. The molecular orbitals reported in the literature are the fully delocalised ones which have substantial amplitudes at all or many positions in the molecule. This set of molecular orbitals may be replaced, without altering the physical reality of the complete wave function, by an equivalent set of localised molecular orbitals which correspond to the two-electron bonds and the lone pairs used in chemical thinking. When the wave function has been obtained in this form, the hybridisations in the individual hybrid atomic orbitals can be written down immediately (Part I) and the polarity parameters of the two-electron bond molecular orbitals can be used to deduce the atomic charges (Part II). Further details and references are given in the earlier papers.[1] In two of the examples dealt with here, some localised molecular orbitals were discussed by the original authors [3,4] but, now that sets of localised molecular orbitals are available for some twenty molecules, new comparisons are possible.

TABLE 2.

Dipole moments (D) in the water, ammonia, and formaldehyde molecules.

		$\mu_q(z)$		μ_{LP}	$\mu_B(z)$			μ_T	$\mu_{exp.}$
Water.	(A)	0·68		1·69	0·06			2·43	1·84
	(B)	0·76		3·20	−2·20			1·76	
Ammonia.	(A)	0·75		3·76	−2·02			2·49	1·46
	(B)	0·69		3·52	−1·97			2·24	
	(C)	1·14		3·41	−1·77			2·78	
	(D)	1·08		3·56	−2·34			2·30	
		CH	CO		C→H	C→O	O→C		
Formaldehyde.	(A)	0·66	0·88	1·39	−2·77	1·86	0·63	2·47	2·3
	(B)	0·76	1·00	1·66	−2·37	1·69	0·06	2·62	

$\mu_q(z)$ is the z component of the *total* atomic charge (q) dipole. μ_{LP} is the total hybridisation dipole from the lone pairs. $\mu_B(z)$ is the z component of the *total* hybridisation dipole from all the hybrid atomic orbitals of the two-electron bonds. A positive sign for μ denotes that the dipole is oriented with its negative end uppermost when the molecules are oriented as in Fig. 1. The total calculated moment for formaldehyde (μ_T) includes a π-dipole moment of $-0{\cdot}18$ which is not shown in the other columns of the Table.

Wave functions are available for three non-linear molecules: water,[3] ammonia,[4] and formaldehyde.[5] Ellison and Schull's early wave function [3] for water is not as good as the wave functions for the other molecules of this set.[6] The ammonia molecule has been dealt with twice, by Duncan using Slater atomic orbitals and by Kaplan using Hartree–Fock atomic orbitals for the nitrogen atom.[4] The formaldehyde calculations have also been carried out twice, by Foster and Boys and by Goodfriend, Birss, and Duncan.[5] The wave function reported by the latter authors did not give such well-localised molecular

[3] Ellison and Schull, *J. Chem. Phys.*, 1955, **23**, 2349.

[4] Duncan, *J. Chem. Phys.*, 1957, **27**, 423; Kaplan, *ibid.*, 1957, **27**, 1704.

[5] Foster and Boys, *Rev. Mod. Phys.*, 1960, **32**, 303; Goodfriend, Birss, and Duncan, *ibid.*, 1960, **32**, 309.

[6] McWeeney and Ohno, *Proc. Roy. Soc.*, 1960, *A*, **255**, 367.

orbitals as did that reported by Foster and Boys, although the two sets of results appear to be very much alike. Only Foster and Boys's wave function has been used in this work.

There is one additional factor which arises when dealing with non-linear molecules as compared with linear ones. This is the question of bond angles and straight *versus* bent bonds. The condition that the bonds be straight is effectively another localisation requirement and it has been used in this way for the water and ammonia molecules in this paper.

The results are reported, in the Tables and Figures, in the notation used earlier; [1] this is explained briefly in the footnotes.

DISCUSSION

It is convenient first to examine the three molecules separately.

Water.—This molecule has been dealt with several times.[3,6,7] McWeeney and Ohno's work [6] is the most comprehensive now available. The present results, based on those of Ellison and Schull, cannot be given too much weight because of the deficiencies of the original computation. As a result, the localisation is poor and the hybridisations vary strongly with the localisation route [(A) and (B) in Fig. 1]. The localisation is somewhat better in (A) than in (B) so, if more weight is given to the former result, we can say that the lone pair is close to a pure 2*s*-atomic orbital and that the hybrid atomic orbitals of the two-electron bonds are close to pure $2p\sigma$-atomic orbitals. This is an interpretation which agrees with the results for linear molecules (Part I) and with the idea that the hybridisations in water will be small because the promotion energy of the oxygen atom is quite large.[8]

The atomic charges in the water molecule also agree well with those for the hydroxyl radical and the other linear molecules (Part II). Those in the water molecule should perhaps be increased somewhat, say by 0·04 electron, to correct for localisation deficiencies but the agreement with the results for linear molecules is still good. The dipole moment of the water molecule comes largely, but certainly not completely, from the lone pair.[7] The moments from the atomic charges and those from the hybrid atomic orbitals of the two-electron bonds are also important in determining the total dipole moment. Again, this result is very like those for the linear molecules.

Ammonia.—The localisation here is good and, as a result, the hybridisations do not vary much with the localisation route. In this case, we have the opportunity to compare the hybridisations obtained when using Slater atomic orbitals [(A),(B)] with those obtained with Hartree–Fock atomic orbitals [(C),(D)]. It is interesting that the hybridisations do not vary much between the two sets of atomic orbitals, while the atomic charges do vary substantially.[9] All four localisations show that the lone pair is heavily hybridised ($\sim sp$). This is the only example found so far of such a lone pair. The lone pairs in the nitrogen molecule, in hydrogen cyanide and in cyanogen, are all quite close to pure 2*s*-atomic orbitals (Part I), and the difference between the ammonia lone pair and the lone pairs in these three molecules can be connected, if rather vaguely, with the fact that ammonia is basic while the other molecules are not. This difference between the ammonia lone pair and those of the three linear molecules is not repeated in the two-electron-bond hybrid atomic orbitals of ammonia; these are close to pure $2p\sigma$-atomic orbitals, on the whole, as are the hybrid atomic orbitals of the two-electron bonds of the linear molecules in the isovalent situation.

The atomic charges in ammonia are larger by 50—100% than those in the NH radical (Part II). It is difficult to understand this result. The opposite result might have been expected if a saturation effect were to occur in ammonia, the amount of charge transferred

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[7] Pople, *ibid.*, 1950, *A*, **202**, 323; Pople and Duncan, *Trans. Faraday Soc.*, 1953, **49**, 217.

[8] Cf., Mulliken's estimates for linear molecules, *J. Phys. Chem.*, 1952, **56**, 310.

[9] Peters, *J. Chem. Phys.*, 1962, **36**, 2743.

from hydrogen to nitrogen in each bond being smaller when there are three bonds than when there is only one.

The dipole moment of ammonia again comes mostly from the lone pair [7] but the other moments are of comparable size.

Formaldehyde.—The localisation here is good. The lone pairs on the oxygen atom are close to pure $2s$- and $2p$-atomic orbitals, although the $2s$-like lone pair contains a little of the $2p\sigma$-atomic orbital whose effect is a partial removal of the lone-pair electrons from the binding region. The carbon–oxygen bond is made up of an almost pure $2p\sigma$-atomic orbital on oxygen and a hybrid atomic orbital on carbon, which contains similar amounts of the $2s$- and $2p\sigma$-atomic orbitals. The carbon hybrid atomic orbitals which form the carbon–hydrogen bonds are also heavily hybridised. All of these results agree neatly with those on linear molecules and with our general expectation.

The σ atomic charges in formaldehyde also fit well with the results for linear molecules. Those of the carbon–oxygen σ-bond are the same as those in this bond in carbon dioxide, the oxygen taking 0·15 electron from the carbon. The atomic charges in the carbon–hydrogen bonds of formaldehyde also fit well with those in the carbon–hydrogen bonds of acetylene, hydrogen cyanide, and the CH radical, providing that allowance is made for the variation of the electronegativity of a hybrid atomic orbital with its hybridisation. In the CH radical, there is no charge transfer from hydrogen to carbon because a pure $2p\sigma$-atomic orbital of the carbon atom has the same electronegativity as a hydrogen atom (Part II). In the carbon–hydrogen bonds of acetylene and hydrogen cyanide, where the carbon atom uses the more electronegative sp-hybrid atomic orbital, some 0·21—0·26 electron is transferred to carbon. In formaldehyde the carbon hybrid in the carbon–hydrogen bonds is quite close to sp^2, which should be intermediate in electronegativity between a pure $2p$-atomic orbital and an sp-hybrid. In agreement with this, the charge transfer to carbon is 0·14 electron, intermediate between that in the CH radical and that in acetylene and hydrogen cyanide. It is pleasing to find this regularity connecting atomic charge, electronegativity, and hybridisation because this was an important concept in understanding the results for linear molecules.

The π-atomic charges of formaldehyde are, like the π-atomic charges in the linear molecules, of the unexpected sign. Charge accumulates on carbon rather than on oxygen, although only to a small extent (0·03 electron). From this result, and that for carbon dioxide, it seems that a σ-electron accumulation of about 0·15 electron on oxygen is sufficient to cancel the gross electronegativity of this atom towards the π-electrons and so leave the π-electron distribution non-polar.

The dipole moment of formaldehyde does not come from any one source. The lone-pair dipoles, the atomic-charge dipoles, and the dipoles from the hybrid atomic orbitals, which form the two-electron bonds, are all of comparable size and no simple picture of the origin of the dipole moment is possible. A common assumption, which is quite clearly contradicted, is that the observed dipole moment comes largely from the π-electrons.

General Comments.—It is again clear that there are indeed two-electron bonds and lone pairs in these self-consistent field wave functions. In the ammonia and formaldehyde molecules, the imperfections in the localisation are so small as to suggest that the localised molecular orbitals really have physical meaning. The present results are in one way simpler than those for the linear molecules because the curious negative hybrids do not occur here, except to an insignificant extent in one of the two localisation schemes of formaldehyde (A). It seems safe to say that whatever the shortcomings of Hartree–Fock molecular wave functions may be—and these are not well understood yet—they at least provide a consistent and clear picture of *some* of the factors governing molecular structure. Moreover, this picture agrees well with that deduced on quite different grounds by chemists. It seems reasonable to hope that future modifications of this picture will be quantitative rather than qualitative, even if the results are expressed in a different and more precise language, such as that of density matrices. The most disappointing result is that no simple picture of the origin of molecular dipole moments can be given. It is true that the hybridisations reported here are not as reliable as the atomic charges (Part II), but it would be a remarkable coincidence if the hybridisation dipoles were to disappear when better wave functions are available.

Two major problems which will be dealt with later in this series are the question of energy quantities and that of bond strengths.

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