372. *Localised Molecular Orbitals in the Self-consistent Field Wave Functions of Linear Molecules. Part I. Hybridisations.*

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The delocalised molecular orbitals of the self-consistent field wave functions of some small linear molecules are transformed into molecular orbitals which are almost completely localised and correspond closely to the usual ideas of the lone pair and the two-electron bond. The hybridisation in the hybrid atomic orbitals of the lone pairs and of the two-electron bonds are discussed in this paper.

There is good agreement between the hybridisations deduced here and the more conservative general views on the subject. The lone pairs on the end atoms of the linear molecules are largely $2s$ atomic orbitals and the effect of the small amout of the $2p\sigma$ atomic orbital which they contain is to remove the lone pairs partly from the internuclear region. In the molecular orbitals of the two-electron bonds the hybridisations are small except when an increase in the formal valency of an atom results from the hybridisation; in the latter event the hybridisations are approximately those of the simple sp hybrids.

There are two unexpected results. First, the hybridisation in the hybrid atomic orbitals which form the two-electron bonds is sometimes in the unexpected direction, the hybrid atomic orbital being concentrated away from the internuclear region. Secondly, the hybrid atomic orbitals at a given atom are often far from orthogonal.

It seems to be generally true that the hybridisations in the hybrid atomic orbitals are sensitive to small changes in the wave function. The polarity of the molecular orbitals is relatively insensitive to these small changes. It may be inferred that the total energy is more sensitive to the polarity of the molecular orbitals than to the hybridisations in the hybrid atomic orbitals.

One of the promising developments in the computation of wave functions for large molecules is the utilisation of the chemical fact that individual bonds in molecules have properties which are, to a certain extent, independent of the structure of the rest of the molecule. The use of this general result in the mathematical apparatus of molecular structure theory has been developed by Parr [1] and Boys [2] and their colleagues. They impose the condition of independent bonds from the start of the calculation. Some calculations on the water molecule along these general lines have been reported by McWeeney and Ohno,[3] and Allen and Schull [4] have discussed the general problem of independent bonds.

In this paper, the question is approached from another point of view which has been developed by Coulson [5] and by Lennard-Jones [6] and their colleagues. This method is to take the fully delocalised molecular orbital wave functions and show that these can be transformed into localised molecular orbitals which do correspond to the usual ideas of chemical valency theory. The difficulty which has so far prevented the development of this approach has been the lack of reliable molecular orbital wave functions and, now that these are becoming available, further progress can be made.

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[1] Parks and Paar, *J. Chem. Phys.*, 1958, **28**, 335; 1960, **32**, 1657.
[2] Foster and Boys, *Rev. Mod. Phys.*, 1960, **32**, 296, 300, 303.
[3] McWeeney and Ohno, *Proc. Roy. Soc.*, 1960, *A*, **255**, 367.
[4] Allen and Schull, *J. Chem. Phys.*, 1961, **35**, 1644.
[5] Coulson, *J. Chim. phys.*, 1949, **46**, 198; " Valence," Clarendon Press, Oxford, 1952, pp. 155 *et seq.*
[6] Lennard-Jones, *Proc. Roy. Soc.*, 1949, *A*, **198**, 1, 14, and subsequent papers in this series by Hall. Hurley, and Pople to which reference is made in ref. 8.

The starting point of this work is the results[7] of a number of self-consistent-field computations on some di-, tri-, and tetra-atomic linear molecules. All but one of the molecules contain only elements of the first row of the Periodic Table. These wave functions are approximations to the Hartree–Fock wave functions of the molecules. The individual molecular orbitals are built from linear combinations of the atomic orbitals of the constituent atoms. As usually presented, the wave functions seem to have little connection with the classical ideas of molecular structure theory and it is important to know whether these ideas lose their usefulness at this level of approximation or whether they are contained in the wave functions in a concealed form. To examine this question, it is necessary to carry out certain transformations on the reported wave functions.

These are linear transformations of the set of occupied delocalised molecular orbitals. When the wave function consists of a single determinant of doubly occupied molecular orbitals, as do most of the available wave functions, these transformations are always possible. In picturing them, one thinks of a set of fully delocalised molecular orbitals, all or most of which have substantial amplitudes throughout the molecule. This set is to be replaced by a set of localised molecular orbitals, each of which has an appreciable amplitude only in a special region of the molecule, such as around one nucleus to form a lone pair or between adjacent nuclei to form a two-electron bond. Simple discussions of this procedure have been given by Coulson[5] and Pople.[8] The general expectation is that this will be possible for all molecules in which conjugation is not important.

Theory of Localisation.—To summarise this briefly, suppose that we are considering the wave function of the ground state of a molecule which contains $2n$ electrons. This is a closed-shell situation and the wave function, Ψ, is given, in a common notation, by

$$\Psi = |\phi_1\bar{\phi}_1 \cdots\cdot \phi_n\bar{\phi}_n|. \qquad (1)$$

The molecular orbitals (ϕ) are the delocalised ones usually reported in the literature.[7] Each belongs to an irreducible representation of the symmetry group of the molecule and they form an orthonormal set. These molecular orbitals are written as an n-dimensional row vector, and a linear transformation is applied to give a new set of localised molecular orbitals (ϕ'). ·This process may be written

$$\phi A = \phi'; \; \phi = \phi' A^{-1}; \qquad (2)$$

where A is an $n \times n$ matrix with a non-vanishing determinant. Then the wave function

$$\Psi' = |\phi_1'\bar{\phi}_1' \cdots\cdot \phi_n'\bar{\phi}_n'| \qquad (3)$$

differs from the original wave function (Ψ) by at most a multiplicative constant.[9] Physically, the two wave functions, Ψ and Ψ', are identical.

In the examples discussed in this paper, all the wave functions are real. If we require that the new molecular orbitals be real and also form an orthonormal set, then the transforming matrix A must be a real orthogonal matrix. Only transformations of this kind will be dealt with in this paper, apart from some comments on non-orthogonal transformations in a later paragraph.

Localised Molecular Orbitals and Hybridisation Parameters.—The delocalised molecular orbitals are written

$$\phi_i = \sum_{r_a} c_i(r_a)\chi_{r_a}, \qquad (4)$$

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[7] (*a*) Ransil, *Rev. Mod. Phys.*, 1960, **32**, 245; (*b*) McLean, *J. Chem. Phys.*, 1960, **32**, 1595; (*c*) Clementi, Technical Report, LMSS, Univ. Chicago, 1959—60, 341; (*d*) Krauss, *J. Chem. Phys.*, 1958, **28**, 1021; (*e*) Clementi, *ibid.*, 1962, **36**, 750; (*f*) Clementi and McLean, *ibid.*, p. 563; (*g*) Clementi, *J. Amer. Chem. Soc.*, 1961, **83**, 4501; (*h*) McLean, personal communication; (*j*) Clementi and McLean, *J. Chem. Phys.*, 1962, **36**, 45.

[8] Pople, *Quart. Rev.*, 1957, **11**, 273.

[9] Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

where χ_{r_a} is the r'th atomic orbital of atom a, i is the molecular orbital label, and $c_i(r_a)$ is the linear coefficient of χ_{r_a} in the molecular orbital ϕ_i. The localised molecular orbitals are written

$$\phi_i' = \sum_{r_a} c_i'(r_a)\chi_{r_a}. \tag{5}$$

The prime distinguishes the localised from the delocalised quantities. We are concerned only with the $1s$, $2s$, and $2p\sigma$ atomic orbitals. The π-electrons which are present in some of these molecules play no further part in the present discussion because the additional transformations involving these electrons [8] give no new results here.

There are two kinds of localised molecular orbitals, lone pairs and two-electron-bond molecular orbitals. A lone pair is a simple hybrid atomic orbital and is written $\lambda_i(\mathrm{a})$. It has the form

$$\lambda_i(\mathrm{a}) = c_i'(2s_a)2s_a + c_i'(2p\sigma_a)2p\sigma_a. \tag{6}$$

The label i now serves to distinguish different lone pairs on atom a. It is convenient to write expression (6) in the form

$$\lambda_i(\mathrm{a}) = h_i(\mathrm{a})2s_a + \{1 - [h_i(\mathrm{a})]^2\}^{1/2}\, 2p\sigma_a. \tag{6'}$$

Now $h_i(\mathrm{a})$ denotes the hybridisation parameter of the i'th lone pair on atom a.

The molecular orbital of a two-electron bond between atoms a and b is written $\mu_j(\mathrm{ab})$ where

$$\mu_j(\mathrm{ab}) = c_j'(2s_a)2s_a + c_j'(2p\sigma_a)2p\sigma_a + c_j'(2s_b)2s_b + c_j'(2p\sigma_b)2p\sigma_b. \tag{7}$$

This may be contracted to

$$\mu_j(\mathrm{ab}) = \mathrm{p}_j(\mathrm{a})hy_j(\mathrm{a}) + \mathrm{p}_j(\mathrm{b})hy_j(\mathrm{b}), \tag{8}$$

where $hy_j(\mathrm{a})$ and $hy_j(\mathrm{b})$ are normalised hybrid atomic orbitals on atoms a and b. Then

$$hy_j(\mathrm{a}) = [\mathrm{p}_j(\mathrm{a})]^{-1}[c_j'(2s_a)2s_a + c_j'(2p\sigma_a)2p\sigma_a] \tag{9}$$

$$= h_j(\mathrm{a})2s_a + \{1 - [h_j(\mathrm{a})]^2\}^{1/2}2p\sigma_a. \tag{10}$$

The label j now distinguishes different bonds between atoms a and b. The terms $\mathrm{p}_j(\mathrm{a})$ and $\mathrm{p}_j(\mathrm{b})$ determine the polarity of the molecular orbital and these quantities are discussed

TABLE 1.

Localised MO's of homonuclear diatomic molecules.*†

$\mathrm{Li_2}$: $^1\Sigma_g^+\,(\mathrm{BMO})^2$
BMO $= 0{\cdot}5310[0{\cdot}9747(2s_a + 2s_b) + 0{\cdot}2233(2p\sigma_a + 2p\sigma_b)]$.
The localisation is perfect.

$\mathrm{N_2}$: $^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{LP_a})^2(\mathrm{LP_b})^2(\pi_u)^4$
BMO $= 0{\cdot}5941[0{\cdot}1097(2s_a + 2s_b) + 0{\cdot}9940(2p\sigma_a + 2p\sigma_b)]$.
$\mathrm{LP_a} = 1{\cdot}0171[0{\cdot}9291(2s_a) - 0{\cdot}3697(2p\sigma_a)] - 0{\cdot}0759(2s_b)$.
$\mathrm{LP_b}$ is identical with $\mathrm{LP_a}$.
This example is discussed in detail in the Appendix.

$\mathrm{F_2}$: $^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{LP_a})^2(\mathrm{LP_b})^2(\pi_u)^4(\pi_g)^4$
BMO $= 0{\cdot}6538[0{\cdot}9990(2p\sigma_a + 2p\sigma_b) - 0{\cdot}0142(2s_a + 2s_b)]$.
$\mathrm{LP_a} = 0{\cdot}9986[0{\cdot}9945(2s_a) - 0{\cdot}1056(2p\sigma_a)] - 0{\cdot}0440(2s_b)$.
$\mathrm{LP_b}$ is identical with $\mathrm{LP_a}$.
The localisation requirement is that the LP's be free from $2p\sigma$ of the other atom. It is not possible to remove completely the $2s$ AO of the other atom from the LP's. The localisation is imperfect.

* The abbreviations used in the Tables are as follows. Hybrid atomic orbital, HAO; bonding molecular orbital, BMO; lone pair, LP. Subscripts are added where necessary to distinguish different lone pairs and bonding molecular orbitals. The $1s$-like molecular orbitals are omitted throughout; they are given in the original references. All hybrid atomic orbitals are written in normalised form.

† The two nuclei are labelled a and b. The positive z-axis points towards the other atom. The basis functions are Slater atomic orbitals.[7a]

TABLE 2.

Localised MO's of heteronuclear diatomic molecules.‡

LiH: ${}^1\Sigma^+(\mathrm{BMO})^2$

$\mathrm{BMO} = 0{\cdot}3934[0{\cdot}8112(2s_{\mathrm{Li}}) + 0{\cdot}5847(2p\sigma_{\mathrm{Li}})] + 0{\cdot}6837(1s_{\mathrm{H}})$.

The localisation is perfect.

BH: ${}^1\Sigma^+(\mathrm{BMO})^2(\mathrm{LP_B})^2$

$\mathrm{BMO} = 0{\cdot}5526[-0{\cdot}2438(2s_{\mathrm{B}}) + 0{\cdot}9698(2p\sigma_{\mathrm{B}})] + 0{\cdot}6554(1s_{\mathrm{H}})$.

$\mathrm{LP_B} = 0{\cdot}9656(2s_{\mathrm{B}}) - 0{\cdot}2577(2p\sigma_{\mathrm{B}})$.

The localisation requirement is that the LP be free from $1s_{\mathrm{H}}$. The localisation is perfect.

CH: ${}^2\Pi(\mathrm{BMO})^2(\mathrm{LP_C})^2(2p\pi_{\mathrm{C}})$

$\mathrm{BMO} = 0{\cdot}6275[-0{\cdot}2940(2s_{\mathrm{C}}) + 0{\cdot}9558(2p\sigma_{\mathrm{C}})] + 0{\cdot}6255(1s_{\mathrm{H}})$.

$\mathrm{LP_C} = 0{\cdot}9840(2s_{\mathrm{C}}) - 0{\cdot}1773(2p\sigma_{\mathrm{C}})$.

The localisation requirement is that the LP be free from $1s_{\mathrm{H}}$. The localisation is perfect.

NH: ${}^3\Sigma^-(\mathrm{BMO})^2(\mathrm{LP_N})^2(\pi^+)(\pi^-)$

$\mathrm{BMO} = 0{\cdot}6701[-0{\cdot}3055(2s_{\mathrm{N}}) + 0{\cdot}9522(2p\sigma_{\mathrm{N}})] + 0{\cdot}6114(1s_{\mathrm{H}})$.

$\mathrm{LP_N} = 0{\cdot}9910(2s_{\mathrm{N}}) - 0{\cdot}1331(2p\sigma_{\mathrm{N}})$.

The localisation requirement is that the LP be free from $1s_{\mathrm{H}}$. The localisation is perfect.

OH: ${}^2\Pi(\mathrm{BMO})^2(\mathrm{LP_O})^2(\pi^+)^2(\pi^-)$

$\mathrm{BMO} = 0{\cdot}6980[-0{\cdot}2908(2s_{\mathrm{O}}) + 0{\cdot}9568(2p\sigma_{\mathrm{O}})] + 0{\cdot}5997(1s_{\mathrm{H}})$.

$\mathrm{LP_O} = 0{\cdot}9937(2s_{\mathrm{O}}) - 0{\cdot}1112(2p\sigma_{\mathrm{O}})$.

The localisation requirement is that the LP be free from $1s_{\mathrm{H}}$. The localisation is perfect.

FH: ${}^1\Sigma^+(\mathrm{BMO})^2(\mathrm{LP_F})^2(\pi^+)^2(\pi^-)^2$

$\mathrm{BMO} = 0{\cdot}7137[-0{\cdot}2770(2s_{\mathrm{F}}) + 0{\cdot}9609(2p\sigma_{\mathrm{F}})] + 0{\cdot}5976(1s_{\mathrm{H}})$.

$\mathrm{LP_F} = 0{\cdot}9951(2s_{\mathrm{F}}) - 0{\cdot}0971(2p\sigma_{\mathrm{F}})$.

The localisation requirement is that the $\mathrm{LP_F}$ be free from $1s_{\mathrm{H}}$. The localisation is perfect.

CO: ${}^1\Sigma^+(\mathrm{BMO})^2(\mathrm{LP_O})^2(\mathrm{LP_C})^2(1\pi)^4$

There are two similar sets (A, B), each of two LPs and one BMO, because there are two ways of localising the delocalised MOs.

(A) $\mathrm{BMO} = 0{\cdot}4573[0{\cdot}0318(2s_{\mathrm{C}}) + 0{\cdot}9995(2p\sigma_{\mathrm{C}})] + 0{\cdot}7267[0{\cdot}1845(2s_{\mathrm{O}}) + 0{\cdot}9828(2p\sigma_{\mathrm{O}})]$.

$\mathrm{LP_O} = 1{\cdot}0311[0{\cdot}9356(2s_{\mathrm{O}}) - 0{\cdot}3550(2p\sigma_{\mathrm{O}})] - 0{\cdot}1410(2s_{\mathrm{C}})$.

$\mathrm{LP_C} = 0{\cdot}9522(2s_{\mathrm{C}}) - 0{\cdot}3787(2p\sigma_{\mathrm{C}})$.

The localisation requirement is that the $\mathrm{LP_C}$ be free from $2s_{\mathrm{O}}$ and $2p\sigma_{\mathrm{O}}$.

(B) $\mathrm{BMO} = 0{\cdot}4401[0{\cdot}1858(2s_{\mathrm{C}}) + 0{\cdot}9826(2p\sigma_{\mathrm{C}})] + 0{\cdot}7548[0{\cdot}0081(2s_{\mathrm{O}}) + 0{\cdot}9999(2p\sigma_{\mathrm{O}})]$.

$\mathrm{LP_O} = 0{\cdot}9629(2s_{\mathrm{O}}) - 0{\cdot}2697(2p\sigma_{\mathrm{O}})$.

$\mathrm{LP_C} = 1{\cdot}0175[0{\cdot}9167(2s_{\mathrm{C}}) - 0{\cdot}3996(2p\sigma_{\mathrm{C}})] - 0{\cdot}1444(2s_{\mathrm{O}})$.

The localisation requirement is that the $\mathrm{LP_O}$ be free from $2s_{\mathrm{O}}$ and $2p\sigma_{\mathrm{C}}$.

LiF: ${}^1\Sigma^+(\mathrm{BMO})^2(\mathrm{LP_F})^2(1\pi)^4$

There are two similar sets (A, B) each of one BMO and one $\mathrm{LP_F}$, because there are two ways of localising the MOs.

(A) $\mathrm{BMO} = 0{\cdot}1707[0{\cdot}7568(2s_{\mathrm{Li}}) + 0{\cdot}6537(2p\sigma_{\mathrm{Li}})] + 0{\cdot}9506[0{\cdot}2924(2s_{\mathrm{F}}) + 0{\cdot}9563(2p\sigma_{\mathrm{F}})]$.

$\mathrm{LP_F} = 1{\cdot}0255[0{\cdot}9035(2s_{\mathrm{F}}) - 0{\cdot}4285(2p\sigma_{\mathrm{F}})] + 0{\cdot}0157(2p\sigma_{\mathrm{Li}})$.

The localisation requirement is that the $\mathrm{LP_F}$ be free from $2s_{\mathrm{Li}}$.

(B) $\mathrm{BMO} = 0{\cdot}1704[0{\cdot}7506(2s_{\mathrm{Li}}) + 0{\cdot}6610(2p\sigma_{\mathrm{Li}})] + 0{\cdot}9411[0{\cdot}4296(2s_{\mathrm{F}}) + 0{\cdot}9030(2p\sigma_{\mathrm{F}})]$.

$\mathrm{LP_F} = 1{\cdot}0035[0{\cdot}8758(2s_{\mathrm{F}}) - 0{\cdot}4827(2p\sigma_{\mathrm{F}})] - 0{\cdot}0180(2s_{\mathrm{Li}})$.

The localisation requirement is that the $\mathrm{LP_F}$ be free from $2p\sigma_{\mathrm{Li}}$.

‡ The positive z-axis points towards the other atom. The basis functions are Slater atomic orbitals.[7a, d]

TABLE 3.

Localised MO's of linear triatomic molecules.§

CO_2: ${}^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{BMO})^2(\mathrm{LP_O})^2(\mathrm{LP_{O'}})^2(\pi_u)^4(\pi_g)^4$

$\mathrm{BMO} = 0{\cdot}6841[-0{\cdot}2823(2s_\mathrm{O}) + 0{\cdot}9593(2p\sigma_\mathrm{O})] + 0{\cdot}5821[0{\cdot}7522(2s_\mathrm{C}) - 0{\cdot}6589(2p\sigma_\mathrm{C})] - 0{\cdot}0789(2s_\mathrm{O'}) + 0{\cdot}0368(2p\sigma_\mathrm{O'})$.

$\mathrm{LP_O} = 0{\cdot}9983[0{\cdot}9820(2s_\mathrm{O}) - 0{\cdot}1886(2p\sigma_\mathrm{O})] + 0{\cdot}0135(2s_\mathrm{O'}) - 0{\cdot}0800(2p\sigma_\mathrm{O'})$.

The localisation requirement is that the lone pairs on oxygen be free from $2s_\mathrm{C}$ and $2p\sigma_\mathrm{C}$.

COS: ${}^1\Sigma^+\,(\mathrm{BMO_{CO}})^2(\mathrm{BMO_{CS}})^2(\mathrm{LP_O})^2(\mathrm{LP_S})^2(\pi_u)^4(\pi_g)^4$

$\mathrm{BMO_{CO}} = 0{\cdot}5310[0{\cdot}7549(2s_\mathrm{C}) + 0{\cdot}6559(2p\sigma_\mathrm{C})] + 0{\cdot}7100[-0{\cdot}2026(2s_\mathrm{O}) - 0{\cdot}9792(2p\sigma_\mathrm{O})] - 0{\cdot}0606(3s_\mathrm{S})$.

$\mathrm{BMO_{CS}} = 0{\cdot}4165[-0{\cdot}3018(3s_\mathrm{S}) + 0{\cdot}9534(3p\sigma_\mathrm{S})] + 0{\cdot}7780[0{\cdot}7586(2s_\mathrm{C}) - 0{\cdot}6515(2p\sigma_\mathrm{C})] - 0{\cdot}0542(2s_\mathrm{O}) + 0{\cdot}0926(2p\sigma_\mathrm{O})$.

$\mathrm{LP_O} = 1{\cdot}0239[0{\cdot}9792(2s_\mathrm{O}) + 0{\cdot}2028(2p\sigma_\mathrm{O})] + 0{\cdot}0476(3p\sigma_\mathrm{S})$.

$\mathrm{LP_S} = 1{\cdot}0382[0{\cdot}9584(3s_\mathrm{S}) - 0{\cdot}2851(3p\sigma_\mathrm{S})] + 0{\cdot}0316(2s_\mathrm{O}) - 0{\cdot}0733(2p\sigma_\mathrm{O})$.

The localisation requirements are that the $\mathrm{LP_O}$ be free from $3s_\mathrm{S}$, $2s_\mathrm{C}$, and $2p\sigma_\mathrm{C}$, that $\mathrm{LP_S}$ be free from $2s_\mathrm{C}$ and $2p\sigma_\mathrm{C}$, and that the $\mathrm{BMO_{CO}}$ be free from $3p\sigma_\mathrm{S}$. There are many other possible localisation routes which have not been explored.

C_3: ${}^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{BMO})^2(\mathrm{LP_a})^2(\mathrm{LP_c})^2(\pi_u)^4$

$\mathrm{BMO} = 0{\cdot}5847[-0{\cdot}2406(2s_\mathrm{a}) + 0{\cdot}9705(2p\sigma_\mathrm{a})] + 0{\cdot}6626[0{\cdot}7927(2s_\mathrm{b}) - 0{\cdot}6096(2p\sigma_\mathrm{b})] - 0{\cdot}1637(2s_\mathrm{c}) + 0{\cdot}0312(2p\sigma_\mathrm{c})$.

$\mathrm{LP_a} = 0{\cdot}9973[0{\cdot}9615(2s_\mathrm{a}) - 0{\cdot}2747(2p\sigma_\mathrm{a})] - 0{\cdot}0031(2s_\mathrm{c}) - 0{\cdot}0501(2p\sigma_\mathrm{c})$.

The localisation requirement is that the LP's be free from $2s_\mathrm{b}$ and $2p\sigma_\mathrm{b}$.

N_3^-: ${}^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{BMO})^2(\mathrm{LP_a})^2(\mathrm{LP_c})^2(\pi_u)^4(\pi_g)^4$

$\mathrm{BMO} = 0{\cdot}5195[-0{\cdot}3603(2s_\mathrm{a}) + 0{\cdot}9328(2p\sigma_\mathrm{a})] + 0{\cdot}7271\,[0{\cdot}7311(2s_\mathrm{b}) - 0{\cdot}6820(2p\sigma_\mathrm{b})] - 0{\cdot}0879(2s_\mathrm{c}) + 0{\cdot}0353(2p\sigma_\mathrm{c})$

$\mathrm{LP_a} = 0{\cdot}9948[0{\cdot}9580(2s_\mathrm{a}) - 0{\cdot}2871(2p\sigma_\mathrm{a})] + 0{\cdot}0083(2s_\mathrm{c}) - 0{\cdot}0624(2p\sigma_\mathrm{c})$.

The localisation requirement is that the LP's be free from $2s_\mathrm{b}$ and $2p\sigma_\mathrm{b}$.

NO_2^+: ${}^1\Sigma_g^+\,(\mathrm{BMO})^2(\mathrm{BMO})^2(\mathrm{LP_O})^2(\mathrm{LP_{O'}})^2(\pi_u)^4(\pi_g)^4$

$\mathrm{BMO} = 0{\cdot}7068[0{\cdot}7731(2s_\mathrm{N}) + 0{\cdot}6342(2p\sigma_\mathrm{N})] + 0{\cdot}5859\,[-0{\cdot}4363(2s_\mathrm{O'}) - 0{\cdot}8998(2p\sigma_\mathrm{O'})] - 0{\cdot}0910(2s_\mathrm{O}) - 0{\cdot}0682(2p\sigma_\mathrm{O})$.

$\mathrm{LP_{O'}} = 0{\cdot}9846(2s_\mathrm{O'}) + 0{\cdot}1473(2p\sigma_\mathrm{O'}) + 0{\cdot}0727(2p\sigma_\mathrm{O}) + 0{\cdot}0042(2s_\mathrm{O})$.

The localisation requirement is that the LP's be free from $2s_\mathrm{N}$ and $2p\sigma_\mathrm{N}$.

HCN: ${}^1\Sigma^+\,(\mathrm{BMO_{CH}})^2(\mathrm{BMO_{CN}})^2(\mathrm{LP_N})^2(\pi_u)^4$

$\mathrm{BMO_{CH}} = 0{\cdot}6560[0{\cdot}7302(2s_\mathrm{C}) - 0{\cdot}6833(2p\sigma_\mathrm{C})] + 0{\cdot}4155(1s_\mathrm{H}) - 0{\cdot}0811(2s_\mathrm{N})$.

$\mathrm{BMO_{CN}} = 0{\cdot}5454[0{\cdot}7203(2s_\mathrm{C}) + 0{\cdot}6936(2p\sigma_\mathrm{C})] + 0{\cdot}6680[-0{\cdot}1343(2s_\mathrm{N}) - 0{\cdot}9909(2p\sigma_\mathrm{N})] - 0{\cdot}0711(1s_\mathrm{H})$.

$\mathrm{LP_N} = 1{\cdot}0166[0{\cdot}9587(2s_\mathrm{N}) + 0{\cdot}2480(2p\sigma_\mathrm{N})] + 0{\cdot}0719(1s_\mathrm{H})$.

The localisation requirement is that the $\mathrm{LP_N}$ be free from $2s_\mathrm{C}$ and $2p\sigma_\mathrm{C}$ and that the $\mathrm{BMO_{CH}}$ be free from $2p\sigma_\mathrm{N}$.

§ The positive *z*-axis points to the right. In carbon dioxide,[7b] the right-hand oxygen is labelled with a prime. In C_3[7j] and N_3^-,[7c] the nuclei are labelled a, b, c from left to right. In hydrogen cyanide,[7h] the nitrogen atom is to the right. In carbon oxysulphide,[7e] the oxygen is to the right. The carbon dioxide, carbon oxysulphide, N_3^-, and NO_2^+, basis-set atomic orbitals are the best atom atomic orbitals. The C_3 basis-set atomic orbitals are the atomic orbitals found [7a] best for a C_2 calculation.

in the following paper. In the same way as before, the $h_j(\mathrm{a})$ and the $h_j(\mathrm{b})$ are the hybridisation parameters of the hybrid atomic orbitals.

The wave function of the molecule may now be written, with omission of the 1*s* atomic orbitals and any π-molecular orbitals, as

$$\Psi' = |\cdot\cdot\cdot\cdot\ \lambda_i(\mathrm{a})\bar{\lambda}_i(\mathrm{a})\ \cdot\cdot\cdot\cdot\ \mu_j(\mathrm{ab})\bar{\mu}_j(\mathrm{ab})\ \cdot\cdot\cdot\cdot|. \tag{11}$$

The quantities $[h_i(\mathrm{a})]^2$ and $\{1 - [h_i(\mathrm{a})]^2\}$ will be referred to as the amount of 2*s* and 2*p*σ character in the hybrid atomic orbital in the usual way.

We can now tentatively define the *total hybridisation*, $H_\mathrm{a}(2\mathrm{s})$ and $H_\mathrm{a}(2p\sigma)$ at atom a by the equations

$$H_\mathrm{a}(2s) = \sum_i 2[h_i(\mathrm{a})]^2 + \sum_j [h_j(\mathrm{a})]^2$$

and

$$H_\mathrm{a}(2p\sigma) = \sum_i 2\{1 - [h_i(\mathrm{a})]^2\} + \sum \{1 - [h_j(\mathrm{a})]^2\}. \tag{12}$$

In both equations, the first summation is over the hybrid atomic orbitals of the lone pairs, and the second is over the hybrid atomic orbitals of the molecular orbitals of the two-electron bond. These total hybridisations are defined in the usual way, but it is important to notice that they are based on hybrid atomic orbitals which are, in general, somewhat non-orthogonal. These quantities will not be used much in this paper, but it is necessary to introduce them at this stage and to record the difference between them and the promotion [10] of an atom. The latter quantity includes charge-transfer effects, while the total hybridisation does not. From this point, some rather complicated questions about the nature of the atom in the molecule arise, but these will not be taken up here.

It is useful to distinguish two kinds of hybrid atomic orbitals, the positive and the negative hybrids.[11] If the coefficients of the $2s$ and the $2p\sigma$ atomic orbitals in a hybrid atomic orbital are both of the same sign,[12] the hybrid is positive. If they are of opposite sign, the hybrid is negative. The signs of the coefficients of the $2p\sigma$ ($\equiv 2pz$) atomic orbitals are determined by the choice of the positive z-axis. The positive z-axes are chosen separately for each hybrid in such a way as to make the expected hybrid

TABLE 4.

Localised MO's of linear tetra-atomic molecules.¶

C_2H_2: ${}^1\Sigma_g{}^+\,(\mathrm{BMO})^2(\mathrm{BMO})^2(\mathrm{BMO})^2(\pi_u)^4$

There are four sets (A, B, C, D) of localised MOs.

(A) $\mathrm{BMO_{CC'}} = 0\cdot5160[0\cdot7788(2s_{\mathrm{C}} + 2s_{\mathrm{C'}}) + 0\cdot6273(2p\sigma_{\mathrm{C}} - 2p\sigma_{\mathrm{C'}})]$.
$\mathrm{BMO_{CH}} = 0\cdot6330[0\cdot6133(2s_{\mathrm{C}}) - 0\cdot7899(2p\sigma_{\mathrm{C}})] + 0\cdot4403(1s_{\mathrm{H}}) + 0\cdot0234(1s_{\mathrm{H'}}) - 0\cdot0594(2s_{\mathrm{C'}}) + 0\cdot0578(2p\sigma_{\mathrm{C'}})$.

The localisation requirement is that $\mathrm{BMO_{CC'}}$ be free from $(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$.

(B) $\mathrm{BMO_{CC'}} = 0\cdot5275[0\cdot6439(2s_{\mathrm{C}} + 2s_{\mathrm{C'}}) + 0\cdot7651(2p\sigma_{\mathrm{C}} - 2p\sigma_{\mathrm{C'}})] - 0\cdot0733(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$.
$\mathrm{BMO_{CH}} = 0\cdot6289[0\cdot7118(2s_{\mathrm{C}}) - 0\cdot7023(2p\sigma_{\mathrm{C}})] + 0\cdot4344(1s_{\mathrm{H}}) + 0\cdot0172(1s_{\mathrm{H'}}) - 0\cdot0012(2p\sigma_{\mathrm{C'}})$.

The localisation requirement is that $\mathrm{BMO_{CH}}$ be free from $2s_{\mathrm{C'}}$.

(C) $\mathrm{BMO_{CC'}} = 0\cdot5275[0\cdot6465(2s_{\mathrm{C}} + 2s_{\mathrm{C'}}) + 0\cdot7629(2p\sigma_{\mathrm{C}} - 2p_{\mathrm{C'}})] - 0\cdot0722(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$.
$\mathrm{BMO_{CH}} = 0\cdot6290[0\cdot7100(2s_{\mathrm{C}}) - 0\cdot7042(2p\sigma_{\mathrm{C}})] + 0\cdot4346(1s_{\mathrm{H}}) + 0\cdot0174(1s_{\mathrm{H'}}) - 0\cdot0010(2s_{\mathrm{C'}})$.

The localisation requirement is that $\mathrm{BMO_{CH}}$ be free from $2\mathrm{p}\sigma_{\mathrm{C'}}$.

(D) $\mathrm{BMO_{CC'}} = 0\cdot5311[0\cdot4907(2s_{\mathrm{C}} + 2s_{\mathrm{C'}}) + 0\cdot8714(2p\sigma_{\mathrm{C}} - 2p\sigma_{\mathrm{C'}})] - 0\cdot1426(1s_{\mathrm{H}} + 1s_{\mathrm{H'}})$.
$\mathrm{BMO_{CH}} = 0\cdot6200[0\cdot7992(2s_{\mathrm{C}}) - 0\cdot6011(2p\sigma_{\mathrm{C}})] + 0\cdot4172(1s_{\mathrm{H}}) + 0\cdot0479(2s_{\mathrm{C'}}) - 0\cdot0702(2p\sigma_{\mathrm{C'}})$.

The localisation requirement is that $\mathrm{BMO_{CH}}$ be free from $1s_{\mathrm{H'}}$.

C_2N_2: ${}^1\Sigma_g{}^+\,(\mathrm{BMO_{CC'}})^2(\mathrm{BMO_{CN}})^2(\mathrm{BMO_{C'N'}})^2(\mathrm{LP_N})^2(\mathrm{LP_{N'}})^2(\pi_u)^4(\pi_g)^4$
$\mathrm{BMO_{CC'}} = 0\cdot5344[0\cdot7028(2s_{\mathrm{C}} + 2s_{\mathrm{C'}}) + 0\cdot7114(2p\sigma_{\mathrm{C}} - 2p\sigma_{\mathrm{C'}})]$.
$\mathrm{BMO_{CN}} = 0\cdot6621[-0\cdot1610(2s_{\mathrm{N}}) + 0\cdot9870(2p\sigma_{\mathrm{N}})] + 0\cdot5572\,[0\cdot7094(2s_{\mathrm{C}}) - 0\cdot7047(2p\sigma_{\mathrm{C}})] + 0\cdot0114(2s_{\mathrm{N'}}) - 0\cdot0187(2p\sigma_{\mathrm{N'}}) - 0\cdot0519(2s_{\mathrm{C'}}) + 0\cdot0403(2p\sigma_{\mathrm{C'}})$.
$\mathrm{LP_N} = 1\cdot0222[0\cdot9592(2s_{\mathrm{N}}) - 0\cdot2829(2p\sigma_{\mathrm{N}})] - 0\cdot0003(2s_{\mathrm{N'}}) + 0\cdot0032(2p\sigma_{\mathrm{N'}}) - 0\cdot0309(2p\sigma_{\mathrm{C}}) - 0\cdot0289(2p\sigma_{\mathrm{C'}}) - 0\cdot0393(2s_{\mathrm{C}} + 2s_{\mathrm{C'}})$.

The localisation requirement is that the $\mathrm{BMO_{CC'}}$ bond be free from $2s_{\mathrm{N}}$ and $2p\sigma_{\mathrm{N}}$.

C_4: ${}^3\Sigma_g{}^-\,(\mathrm{BMO_{ab}})^2(\mathrm{BMO_{cd}})^2(\mathrm{BMO_{bc}})^2(\mathrm{LP_a})^2(\mathrm{LP_d})^2(\pi_u)^4(\pi_u{}^+)(\pi_g{}^-)$
$\mathrm{BMO_{ab}} = 0\cdot7331[-0\cdot5030(2s_{\mathrm{a}}) + 0\cdot8643(2p\sigma_{\mathrm{a}})] + 0\cdot6849[0\cdot7834(2s_{\mathrm{b}}) - 0\cdot6215(2p\sigma_{\mathrm{b}})] - 0\cdot1685(2s_{\mathrm{C}}) - 0\cdot4256(2p\sigma_{\mathrm{b}}) + 0\cdot0791(2p\sigma_{\mathrm{c}}) - 0\cdot0912(2p\sigma_{\mathrm{d}})$.
$\mathrm{BMO_{bc}} = 0\cdot5463[0\cdot8501(2s_{\mathrm{b}} + 2s_{\mathrm{c}}) + 0\cdot5266(2p\sigma_{\mathrm{b}} - 2p\sigma_{\mathrm{c}})]$.
$\mathrm{LP_a} = 0\cdot9616[0\cdot9850(2s_{\mathrm{a}}) - 0\cdot1725(2p\sigma_{\mathrm{a}})] - 0\cdot0305(2s_{\mathrm{d}}) - 0\cdot0209(2p\sigma_{\mathrm{d}}) + 0\cdot0021(2s_{\mathrm{b}} - 2s_{\mathrm{c}}) - 0\cdot0434(2p\sigma_{\mathrm{b}} + 2p\sigma_{\mathrm{c}})$.

The localisation requirement is that $\mathrm{BMO_{bc}}$ be free from $2s_{\mathrm{a}}$, $2s_{\mathrm{d}}$, $2p\sigma_{\mathrm{a}}$, and $2p\sigma_{\mathrm{d}}$.

¶ The positive z-axis points to the right. The primed atoms of acetylene [7b] and cyanogen [7f] are to the right. The basis-set atomic orbitals of acetylene and cyanogen are the best atom atomic orbitals, and the C_4 basis set are the atomic orbitals found best for C_2.[7a]

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[10] Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338, 2343.

[11] Mulliken, *J. Chem. Phys.*, 1951, **19**, 900.

[12] Moffitt and Coulson, *Phil. Mag.*, 1947, **38**, 634.

the positive one. That is, we expect lone pairs to be concentrated outside the binding region and, when they are, their hybrid atomic orbitals are called positive. Equally, we expect the hybrids of a bonding molecular orbital to be concentrated towards the other atom and so such hybrids are called positive. This is equivalent to choosing the z-axis separately for each hybrid atomic orbital to fit our expectations, and this terminology is used everywhere in this paper save in the Tables where it is convenient to retain (and define) the original authors' choice of positive z-axis.

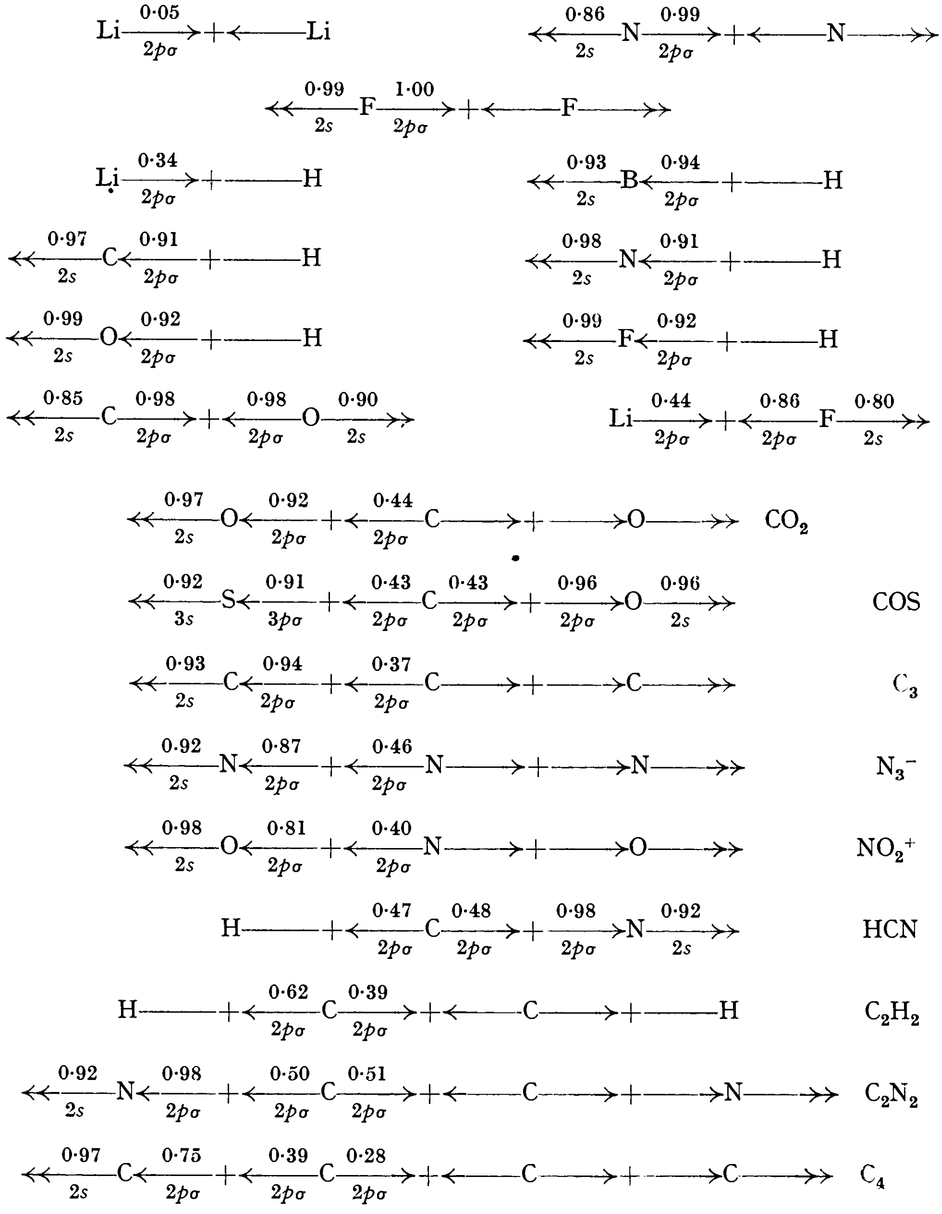
Details of Localisation.—A number of minor points remains to be cleared up. The first of these concerns the completeness of the localisation. It is not in general possible to find an orthogonal transformation which will completely localise all the delocalised molecular orbitals, although this is possible in some special cases. This fact seems to give rise, at first sight, to questions about the uniqueness of the localised molecular orbitals. It transpires, however, in all the cases studied so far, that different localisation routes lead to the same end-point: there is always just one set of localised molecular orbitals. The localisation is not perfect and the degree of imperfection is shown in the Tables. We take the almost localised molecular orbitals and simply delete the imperfections. An example of an imperfection is a small amount of an atomic orbital of another atom in the lone pair hybrid of one atom. The resulting set of molecular orbitals (renormalised, if necessary) is now perfectly localised but slightly non-orthogonal. The Figure was drawn up from this set of molecular orbitals.

It is, in fact, possible to reach the same end-point in another way. If we relax the requirement that the transformation be orthogonal, then it is possible to localise completely all the molecular orbitals. Three examples (nitrogen, fluorine, and carbon monoxide) were examined by this method, the sole relaxation being of the requirement that the two lone pairs be orthogonal. The result in all three cases was the same as that obtained by the earlier method, so this procedure has not been used further.

The 1s atomic orbitals and the low-energy 1s-like molecular orbitals present a problem. It is possible to apply a preliminary transformation to the set of delocalised molecular orbitals and concentrate *all* the 1s atomic orbitals into the low-energy molecular orbitals. On the other hand, it is not generally possible to use this preliminary transformation to remove *all* the 2s and 2$p\sigma$ atomic orbitals from the low-energy molecular orbitals. In the early stages of this work, all calculations were carried out by first orthogonalising the 1s and 2s atomic orbitals of the same atom and then applying the preliminary transformation to removal all the 1s atomic orbitals from the higher-energy, valence, molecular orbitals. All the molecules except hydrogen cyanide, carbon oxysulphide, cyanogen, C_4, and NO_2^+ were dealt with in this way, but in fact the results do not differ significantly from those obtained by simply deleting the 1s atomic orbitals from the valence molecular orbitals. This method was used for the five larger molecules mentioned above.

There is also some choice in the starting set of wave functions. The reported wave functions sometimes differ in the parameters (and occasionally in the functional form) of the atomic orbitals of the basis set. The results based on Slater atomic orbitals (or " best atom " atomic orbitals) have been used because they constitute the largest and most consistent set. These are not the best wave functions of this general type now available, but the improved wave functions, which have modified basis function atomic orbitals, are not so easily handled and different molecules have been treated in different ways when modifying the basis set.

The Table of results shows in each case how the localisation was carried out. The results are reported in a convenient shorthand form in the Figure. In several cases, two or more sets of localised molecular orbitals have been reported in the Tables to show the similarity of sets of localised molecular orbitals obtained in different ways. In some of the larger molecules there are many possible ways of carrying out the localisation, and no attempt has been made to find them all. A detailed example of the localisation of the molecular orbitals of the nitrogen molecule is given in the Appendix.



The arrows are symbols for hybrid atomic orbitals. A single-headed arrow denotes a hybrid atomic orbital which forms a two-electron bond molecular orbital. A double-headed arrow denotes a lone pair. The direction of the arrow shows on which side of the nucleus the hybrid is concentrated. Arrows pointing away from the nucleus denote a positive or normal hybrid, those pointing towards a nucleus denote a negative hybrid. The plus sign denotes that the molecular orbital is bonding. The hybrid atomic orbital of a bonding molecular orbital is characterised by the amount of the 2*p*σ atomic orbital in it: the hybrid atomic orbital of a lone pair is characterised by the amount of the 2*s* atomic orbital in it. These are the numbers written above the arrows and are the squares of the coefficients in equations 6′ and 10.

Where there are two similar localisation procedures, a compromise value is given in the Figure and the exact results are listed in the Tables.

DISCUSSION

It is clear from our results that the two-electron bond and the lone pair are indeed contained in the wave functions of these molecules. The main reservation on this conclusion is that polarisation and distortion of the Slater atomic orbitals were totally neglected in the original computations. Numerical evidence on this point is accumulating now,[13] but it is important to see first how well we can do with the simplest atomic orbital forms.

There are also two points of uncertainty in the present treatment itself. The first is the problem of the 1*s* atomic orbitals and the question of what role they play in bond formation. It seems most unlikely that this point is important. The second problem is the imperfections in the localisation and these may be important. They may arise because it is impossible to represent a molecular wave function to this accuracy in terms of localised molecular orbitals built from atomic orbitals of low principal quantum number. If this is the case, the imperfections are connected with the interactions between isolated bonds. On the other hand, the present wave functions may simply be inaccurate by amounts of the size of the imperfections and then the latter are of no significance. Some further comments on this point are made below.

Hybridisations in Individual Molecules.—It is convenient to think first about some individual molecules and groups of molecules and then to take up some general questions.

In the homonuclear diatomic molecules lithium, nitrogen, and fluorine, there is no charge transfer to complicate the picture and the hybridisations are not extensive. There is no hybridisation whatever in fluorine, and this is reasonable since the fluorine atom's promotion energy is very high.[14] In the nitrogen molecule, there is hybridisation only in the lone pairs, not in the hybrids of the two-electron bond. It is not clear why this should be the case. In the lithium molecule, there is a little hybridisation in the hybrid atomic orbitals which form the two-electron bond. The promotion energy of lithium is low, so hybridisation is energetically cheap, but there is still only 5% of the $2p\sigma$ atomic orbital in the predominantly 2*s* atomic orbitals which form the bond.

The position is rather different in the diatomic hydrides. Here the hybridisation is greater, but still not very large. The notable point is that all the atoms from boron to fluorine use the same hybridisation in the hybrid atomic orbital which forms the bond to hydrogen. The hybridisations in the lone pairs decrease as the electronegativity of the atom boron to fluorine increases. This is reasonable because the promotion energy also increases along this series, so hybridisation becomes progressively more expensive energetically. Why the hybrid atomic orbitals which form the bond do not show the same trend is not clear, but the question of charge transfer does complicate the position. This will be discussed below.

A striking point about the results for diatomic hydrides is that the hybrids which the atoms boron to fluorine use in forming the bond to hydrogen are negative hybrids. It is very difficult to see what is gained by the use of such hybrids. They remove the bonding electrons from the internuclear region, and, further, they put these electrons into the same region of space as the lone-pair electrons. One would certainly expect both effects to increase the total energy of the molecule. Nevertheless, these negative hybrids occur systematically in the same general situation in many of the molecules of this group, so we must suspend judgment on their reality until better wave functions are available.

The two remaining diatomic molecules are carbon monoxide and lithium fluoride. The carbon monoxide molecule is very like the nitrogen molecule in these results, the lone pairs being some 10% hybridised while the hybrids used to form the bond are almost pure $2p\sigma$ atomic orbitals. This is a sensible result because there are many similarities between carbon monoxide and nitrogen. The results for lithium fluoride appear unusual and,

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[13] Clementi, *J. Chem. Phys.*, 1962, **36**, 33.

[14] Mulliken, *J. Phys. Chem.*, 1952, **56**, 295.

since there must be a great deal of charge transfer from lithium to fluorine in this molecule, the individual hybridisations probably have little meaning.

The triatomic molecules hydrogen cyanide, carbon dioxide, carbon oxysulphide, C_3, NO_2^+, and N_3^-, behave like the diatomic ones in so far as their end atoms are concerned. The lone pairs contain at most a few percent of the $2p\sigma$ ($3p\sigma$ for sulphur) atomic orbital and they are concentrated outside the internuclear binding region. The carbon, nitrogen, and sulphur lone pairs are perhaps more heavily hybridised than the oxygen ones, but the difference is small. The hybrid atomic orbitals which the end atoms use in forming their two-electron bonds are largely $2p\sigma$ atomic orbitals, but such hybridisation as there is again gives a negative hybrid. The second-row atom, sulphur, does not behave differently from the first-row atoms. All this is in line with the results for the diatomic molecule.

The interesting feature of the triatomic molecules is the behaviour of the central atom. As we would expect, this atom is alway heavily promoted since it is quadrivalent. In no case, however, does the hybridisation in a hybrid atomic orbital reach the full value for an *sp* hybrid. This is an indication that the atom is not fully promoted to the state which gives two *sp* hybrids for the σ-bond formation, although here again charge transfer and non-orthogonality of hybrid atomic orbitals complicate the position.

Of the three tetra-atomic molecules, acetylene is particularly interesting because it is easy to find four different localisation routes, all of which lead to very similar sets of localised molecular orbitals. These are discussed below. In cyanogen, the localisation is good and it is notable that the hybrid atomic orbitals on the carbon atoms are nearly orthogonal. The C_4 example should not be given too much weight since the experimental bond lengths are not known and estimated values were used in the original computation. In general, the tetra-atomic molecules closely resemble the triatomic ones, having lone pairs on the end atoms which are in largely 2*s* atomic orbitals, little hybridisation in the hybrid atomic orbitals which the end atoms use in forming the bonds, and extensive hybridisation in the hybrid atomic orbitals of the central atoms.

Summary on Hybridisations.—The individual results can be collected in the following generalisations. Hybridisation is extensive only when an increase in the valency of the atom is involved. It is never extensive in the lone pairs of the kind dealt with here. Of the eighteen molecules of this group which have lone pairs, only in nitrogen and carbon monoxide does the amount of $2p\sigma$ atomic orbital in the lone pairs exceed 10% and in these two the localisation is not particularly good. Even this figure is probably too high because it includes an unknown amount of forced hybridisation [15] which arises from the insistence that the molecular orbitals be orthogonal. It is important to notice that this conclusion is valid only when the π electrons are not included in the transformations.

The hybrid atomic orbitals which the atoms use in forming two-electron bonds can be separated clearly into two groups, those of the end atoms and those of internal atoms. The hybrids of the end atoms rarely contain more than 10% of the 2*s* atomic orbital in the predominantly $2p\sigma$ atomic orbitals: two exceptions to this generalisation are the lithium atom hybrids in lithium hydride and lithium fluoride, which can be understood because the promotion energy of lithium is exceptionally low. In so far as the σ electrons are concerned, the end atoms are in the isovalent situation [14] in which an atom forms bonds without increasing its valence over that natural to the free atom. We may form a rough rule that 10% of the 2*s* atomic orbital in the predominantly $2p\sigma$ atomic orbital is about the limit of hybridisation in this circumstance.

The second group is that of internal atoms. The hybrid atomic orbitals which they use in forming their σ bonds are always heavily hybridised. This is the pluvalent situation [14] in which the natural free-atom valence is exceeded when the atom is incorporated into the molecule.

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[15] Mulliken, *J. Chem. Phys.*, 1951, **19**, 912.

These general conclusions are remarkably simple and straightforward despite the wide range of atoms and bond lengths in this set of molecules. If they can be sustained with better wave functions, then numerical justification for some of the simple ideas of molecular structure theory will be available.

The question concerning the non-orthogonality of the hybrid atomic orbitals at an atom is puzzling. It is generally assumed, in the absence of evidence to the contrary, that these hybrids should be taken as orthogonal and this is a basic assumption in much published work. As is shown below, the hybridisation numbers are somewhat uncertain, so the point should not be given too much weight, but it is an alarming result because many of our ideas about the geometry of non-linear molecules are built on the assumption of rigorous orthogonality of the hybrid atomic orbitals of a given atom. The best point of view now is that the hybrid atomic orbitals of an atom tend towards orthogonality but do not necessarily quite reach it. Then we can retain the qualitative idea that molecular angles are determined by the hybridisation at the apex atom, but we need no longer expect these angles to be exactly 90° or 120° in, for example, water and ethylene.

Imperfections in the Localisation.—The results for the acetylene molecule are useful in that it is possible to check the sensitivity of the conclusions to the details of the localisation procedure. The situation in the σ frame of acetylene is that there are three delocalised molecular orbitals, $2\sigma_g$, $3\sigma_g$, and $2\sigma_u$. These are to be localised into two carbon–hydrogen bonds and the carbon–carbon bond. There is only one disposable parameter in this transformation and this has been used as shown in Table 4 to give four distinct sets of almost localised molecular orbitals. It is clear that all four are approximations to one unique set of perfectly localised molecular orbitals. The point is particularly clear from the coefficients with which the carbon hybrid atomic orbital and the hydrogen $1s$ atomic orbital enter the molecular orbital of the carbon–hydrogen bond. These numbers are the polarity parameters of the molecular orbital (eqn. 8) and they are sensibly constant in all four sets of localised molecular orbitals. The hybridisation parameters, on the other hand, change substantially from one set of localised molecular orbitals to another. The results for carbon monoxide and lithium fluoride, in each of which there are two possible localisation schemes, show the same effects. The total hybridisation (eqn. 12) is less sensitive to the localisation route than is the hybridisation in a particular hybrid atomic orbital. It seems, then, that the hybridisation can be switched from one hybrid atomic orbital of an atom to another such hybrid of the same atom without much change in the wave function of the whole molecule. It is then a reasonable inference that the total energy is also rather insensitive to the hybridisation in a particular hybrid atomic orbital. The polarity parameters, on the other hand, affect the total energy critically. For these reasons, it seems likely that the polarity parameters are well determined by these wave functions but that the hybridisation parameters will be finally fixed only by very accurate computations. This situation is the reason for reserving judgment on the reality of the negative hybrids which are found in some of these molecules.

It is interesting that the same point can be made in valence-bond theory. In this theory, it is often supposed that ionic–covalent resonance is the important factor in determining the total energy and that the question of the hybridisation may be ignored to a first approximation. It is easy to show that the hybridisation parameters in a molecular-orbital wave function determine only whether the ionic part of the wave function, for example, uses $2s$ or $2p\sigma$ atomic orbitals. This is clear if we take an isolated two-electron bond, write down its molecular-orbital wave function, and then expand this into the valence bond components in the following way.

$$\begin{aligned}\Psi &= |\mu(\mathrm{ab})\bar{\mu}(\mathrm{ab})| \\ &= |[\mathrm{p}(1)hy(1) + \mathrm{p}(\mathrm{m})hy(\mathrm{m})]\alpha[\mathrm{p}(1)hy(1) + \mathrm{p}(\mathrm{m})hy(\mathrm{m})]\beta| \\ &= [\mathrm{p}(1)]^2|hy(1)\alpha\,.\,hy(1)\beta| + [\mathrm{p}(\mathrm{m})]^2|hy(\mathrm{m})\alpha\,.\,hy(\mathrm{m})\beta| \\ &\qquad + \mathrm{p}(1)\mathrm{p}(\mathrm{m})[|hy(1)\alpha hy(\mathrm{m})\beta| + |hy(\mathrm{m})\alpha hy(1)\beta|]\end{aligned}$$

Only the polarity parameters, p, determine the relative weights of the covalent and ionic forms. This parallelism between molecular-orbital and valence-bond theories seems to be new, but the suggestion about the importance of the polarity parameters in determining the total energy is certainly in line with the valence-bond idea that the ionic–covalent resonance is the important factor in determining the total energy of the molecule. A number of points concerning these polarity parameters are taken up in the following paper.

This work was begun while the author was a member of the Laboratory of Molecular Spectra and Structure in the 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 much advice and discussion on the points in this paper.

APPENDIX

The detailed procedure used to localise the molecular orbitals of the N_2 molecule is as follows. The reported [7a] valence molecular orbitals of nitrogen (after orthogonalisation of the $1s/2s$ atomic orbitals of the same atom and removal of the $1s$ atomic orbital from the valence molecular orbitals) are:

$$2\sigma_g = 0\cdot4745(2s_a + 2s_b) + 0\cdot2391(2p\sigma_a + 2p\sigma_b);$$

$$2\sigma_u = 0\cdot7215(2s_a - 2s_b) - 0\cdot2659(2p\sigma_a - 2p\sigma_b);$$

$$3\sigma_g = 0\cdot3960(2s_a + 2s_b) - 0\cdot6019(2p\sigma_a + 2p\sigma_b).$$

The two nuclei are labelled a and b. The positive z-axes point towards the other atom.

These are to be transformed into an N–N bond and two lone pairs. The N–N bond cannot contain $2\sigma_u$ since it must be symmetrical about the mid-point of the molecule. The matrix element A_{31} is thus zero. The two lone pairs must be identical in form and so contain equal amounts of $2\sigma_g$ and $3\sigma_g$ and also equal amounts of $2\sigma_u$ with opposite sign. These requirements fix the matrix A up to a single disposable parameter, α. The transformation is:

$$2\sigma_g, 3\sigma_g, 2\sigma_u \begin{bmatrix} \cos(\alpha) & \sin(\alpha)/2^{1/2} & \sin(\alpha)/2^{1/2} \\ -\sin(\alpha) & \cos(\alpha)/2^{1/2} & \cos(\alpha)/2^{1/2} \\ 0 & 2^{-1/2} & -2^{-1/2} \end{bmatrix}$$

$$= \text{BMO}, \text{LP}_a, \text{LP}_b$$

or, without matrix notation:

$$\text{BMO} = \cos(\alpha)2\sigma_g - \sin(\alpha)3\sigma_g.$$

$$\text{LP}_a = 2^{-1/2}\sin(\alpha)2\sigma_g + \cos(\alpha)3\sigma_g + 2\sigma_u.$$

$$\text{LP}_b = 2^{-1/2}\sin(\alpha)2\sigma_g + \cos(\alpha)3\sigma_g - 2\sigma_u.$$

Ideally, the lone pair on atom a should be completely free from $2s_b$ and $2p\sigma_b$. This requirement leads to two equations of the form $f\cos(\alpha) + g\sin(\alpha) + h = 0$, where f, g, h are constants. One of these equations, that which would completely remove $2s_b$ from LP_a, has no real solution. The second, which completely removes $2p\sigma_b$ from LP_a, has two real solutions. One of these corresponds to a large amount of $2s_b$ in LP_a, but the second corresponds to only a small amount of $2s_b$ in LP_a. With this value of the parameter α, the localised molecular orbitals, when written in terms of normalised hybrid atomic orbitals, are:

$$\text{BMO} = 0\cdot5941[0\cdot1097(2s_a + 2s_b) + 0\cdot9940(2p\sigma_a + 2p\sigma_b)].$$

$$\text{LP}_a = 1\cdot0171[0\cdot9291(2s_a) - 0\cdot3697(2p\sigma_a)] - 0\cdot0759(2s_b).$$

LP_b is identical with LP_a. The hybridisations are then 99% of $2p\sigma$ in the BMO and 86% of $2s$ in the LP's.

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