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Criteria for Bond Orbitals and Optimum Hybrids

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A prescription is derived for setting up 'optimum hybrids'. A simple localised-orbital wave function, based on these hybrids, gives the closest possible approach to the results of an accurate SCF calculation, the error depending only on constraints imposed on the forms of the hybrids and vanishing when all restrictions are removed. The hybrids describing the bonds and lone pairs in CH_4, H_2O and CH_2O are obtained and discussed.

Eine Vorschrift zur Bestimmung „optimaler Hybride" wird angegeben, und eine einfache Wellenfunktion mit lokalisierten Einelektronenzuständen, die sich aus diesen Hybriden aufbaut, kommt den Ergebnissen einer SCF-Rechnung am nächsten. Der Fehler hängt nur von den Nebenbedingungen, die die Form der Hybride bestimmen, ab und verschwindet, wenn keine derartigen Einschränkungen vorliegen. In diesem Zusammenhang werden die Hybride, die in den Molekülen CH_4, H_2O und CH_2O vorliegen, diskutiert.

On établit une méthode pour construire des «hybrides optima». Une simple fonction d'onde en orbitales localisées, basées sur ces hybrides,donne des résultats aussi voisins que possible de ceux d'un calcul S.C.F. précis, l'erreur ne dépendant que des containtes imposées à la forme des hybrides et disparaissant lorsque ces contraintes sont abolies. On obtient ainsi les hybrides décrivant les liaisons et les paires libres dans CH_4, OH_2 et CH_2O.

1. Introduction

Many prescriptions have been devised recently for extracting a set of localised orbitals from a wave function based on non-localised molecular orbitals (MO's) or for setting up hybrid AO's from which such orbitals may be constructed [1–11]. The general aim is to obtain a more substantial foundation for the description of a molecule in terms of well-established concepts such as inner shells, lone pairs, and bond pairs. It is well known that wave functions recognising the individuality of such units, or "electron groups", in which, for example, bond orbitals are constructed from hybrids pointing along the bond directions, may easily be developed to give ground state energies considerably superior to those derived using approximate self-consistent field (SCF) MO theory [12–16]. But there are many instances – for example when the bonds are "bent" or when there are lone pairs of electrons – in which the forms of the localised orbitals, or of the optimum hybrids from which they may most effectively be constructed, are not intuitively apparent. In such cases there is a special need to formulate mathematical criteria for a "best possible" description in terms of localised orbitals constructed by combining suitable hybrids on adjacent atoms. The hybrids required must be chosen according to a precise definition of "localisation" and according to the use for which they are intended. In particular, the general purpose of the introduction of hybrids and localised orbitals may be (i) that of analysing a given SCF calculation in order to present it in a form more suitable for discussion and application in a chemical context, besides preparing the ground for further improvement (e.g. by configuration interaction); or (ii) that of setting up a basis with certain advantageous features, before even starting a detailed calculation. In the latter case only the simplest properties of the "pure" atomic orbital (AO) basis (e.g. overlap properties) would be used; and some aspects of this approach have already been discussed [2, 4, 6, 7, 10]. On the other hand, the availability of the results of an SCF calculation or of a reliable approximation to it, in terms of the AO basis, permits a more sophisticated analysis leading to hybrids which may be compared with those set up by simpler methods and may offer further guidance in framing appropriate hybridisation criteria. In this paper we focus attention on the direct determination of optimum hybrids with which to reproduce, as closely as possible, the results of a standard SCF MO calculation. The work differs from that of other authors in applying equally well to empirical or non-empirical wave functions, in giving full recognition to the importance of the lone pairs in determining the form of the hybridisation, and in using the total electronic energy as a basic criterion for the optimum hybrids. We stress again the fact that hybridisation is an artificial concept, introduced as an aid to the construction and interpretation of wave functions; different approaches naturally lead to different mathematical prescriptions for obtaining "optimum" hybrids. Here we adopt a point of view which emphasises the special value and convenience of using an orthogonalised orbital basis, with properties which are fully discussed elsewhere [16].

2. Formulation of the Problem

We start from a closed shell one-determinant wave function in which the n orbitals $A, B, C, \dots$ are the non-localised MO's resulting, we may suppose, from an approximate SCF calculation. This approximation is known to yield a good electron density,

$$P(r) = 2 \sum_{U(\mathrm{occ})} U(r)\, U^*(r) \tag{1}$$

and to give a good account of all related one-electron properties, in spite of its failure to include electron correlation in a satisfactory way. The most important type of correlation, that between electrons in localised regions such as bonds, may be introduced later as a refinement; what is important here is to find the forms of the localised orbitals so as to reproduce adequately the properties of the one-determinant approximation.

If the n MO's are expanded in terms of m AO's (basis functions) so that

$$U = \sum_i \phi_i C_{iU} \tag{2}$$

we obtain

$$P(r) = \sum_{i,j} \phi_i(r)\, P_{ij} \phi_j^*(r) \tag{3}$$

where the elements of the $m \times m$ matrix $\boldsymbol{P}$, which are essentially charges and bond orders, are given by

$$P_{ii} = 2 \sum_{U(\mathrm{occ})} |C_{iU}|^2, \qquad P_{ij} = 2 \sum_{U(\mathrm{occ})} C_{iU}\, C_{jU}^* . \tag{4}$$

The energy of the system in one-determinant approximation is then determined entirely by $\boldsymbol{P}$, the variationally best value resulting when

$$E = \operatorname{tr} \boldsymbol{f}\boldsymbol{P} + \tfrac{1}{2} \operatorname{tr} \boldsymbol{G}\boldsymbol{P} = \text{minimum value} \tag{5}$$

where $\boldsymbol{f}$ is the Hamiltonian for an electron in the field of the bare nuclei (or of a core consisting of inner shells), and $\boldsymbol{G}$ is the Roothaan electron-interaction matrix. The SCF equations result from the stationary condition (5) taking due regard to the properties of the matrix $\boldsymbol{P}$ and the fact that $\boldsymbol{G}$ itself depends on the charge density (i.e. on $\boldsymbol{P}$). The first-order change in E, due to a change $\delta\boldsymbol{P}$, is in fact

$$\delta E = \operatorname{tr} \boldsymbol{h}\delta\boldsymbol{P} \tag{6}$$

where

$$\boldsymbol{h} = \boldsymbol{f} + \boldsymbol{G} \tag{7}$$

is the matrix of the Hartree Fock Hamiltonian.

This allows us to write (6) in the equivalent form

$$E_{\text{orb}} = \operatorname{tr} \boldsymbol{h}\boldsymbol{P} = \text{minimum value} \tag{8}$$

in which $\boldsymbol{h}$ is regarded as a *fixed* matrix. In semi-empirical work the self-consistent Hamiltonian $\boldsymbol{h}$ is regarded as a characteristic of the atoms and bonds in the system and its elements are used as disposable parameters, to be identified by appeal to experimental data.

We now turn to the choice of basis orbitals, ϕ_i. Provided we perform a full non-empirical calculation it is irrelevant whether these are ordinary AO's, among which there is substantial non-orthogonality, or whether they are orthogonalised AO's formed by linear combination of the original AO's. It is convenient for our purposes, however, to assume the orbitals orthogonalised, but "closest" to the unmodified AO's in a least squares sense [17]. Such AO's may be set up by well-known methods [18] and according to some criteria at least, appear to have a well-localised character; each contains small parts of the orbitals on other centres, but with signs that ensure cancellation of the parts of the orbitals which trespass on the province of neighbouring atoms[1]. The following treatment can be generalised to apply directly to a non-orthogonal basis, but the prescription for localisation then takes a less convenient form. It therefore appears to be preferable, in the present approach, to perform the calculations in the orthogonal basis: there is no difficulty in making a transformation back to ordinary AO's, at the end of the calculation, and for interpretive purposes this may be desirable. The orthogonal basis has other advantages, particularly in semi-empirical work, in so far as matrix elements defined over orthogonal orbitals are relatively insensitive to changes in molecular environment and neglect of many integrals is permissible [16]. Such a basis will be understood when we refer to the "AO" basis and we shall first of all regard $\boldsymbol{h}$, referred to this basis, as a given matrix representing the "actual" Hartree-Fock operator.

We may, of course, introduce any other basis $\bar{\phi}_1, \bar{\phi}_2, \ldots$, for which the matrices $\boldsymbol{P}$ and $\boldsymbol{h}$ will assume different forms although the total electron density and energy remain invariant. It is important to distinguish this type of invariance from that used by, for example, Lennard-Jones and co-workers [1] who make a unitary

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[1] At first sight the orthogonalised AO's might appear to be more diffuse than the ordinary AO's since small "cusps" appear on neighbouring centres. They are however, on balance, slightly more concentrated in the sense that the electrostatic self-energy integral is invariably *increased* in value by orthogonalising.

transformation of the occupied MO's in order to obtain localised MO's or bond orbitals. Here, on the other hand, we are concerned with the nature of the *basis* orbitals and the question of how they may be chosen so as to facilitate the construction of bond orbitals and lone pair orbitals. Now in simple valence theory it is generally supposed that bond orbitals may be constructed from overlapping pairs of suitably directed hybrid AO's; we shall therefore seek a basis of hybrid AO's in which $\bar{\phi}_r$, $\bar{\phi}_s$, say, overlap to form one bond orbital, $\bar{\phi}_t$ and $\bar{\phi}_u$ to form another, etc., recognising that some of the hybrids ($\bar{\phi}_w, \ldots$) may be without partners and that they then describe lone pairs rather than bonds. The AO basis (ϕ_i) and the hybrid basis ($\bar{\phi}_j$) are related by a transformation matrix $\boldsymbol{T}$ whose columns express the hybrids in terms of AO's

$$\bar{\boldsymbol{\phi}} = \boldsymbol{\phi}\boldsymbol{T} \tag{9}$$

where $\boldsymbol{\phi}$ and $\bar{\boldsymbol{\phi}}$ are row matrices of orbitals. A wave function specified in terms of hybrids will be characterised by a matrix $\bar{\boldsymbol{P}}$, instead of $\boldsymbol{P}$, but the electron density may be expressed in either language using (3) and (9) thus

$$P(r) = \sum_{i,j} \phi_i(r)\, P_{ij} \phi_j^*(r) = \sum_{k,l} \bar{\phi}_k(r)\, \bar{P}_{kl}\, \bar{\phi}_l^*(r) \tag{10}$$

where

$$\boldsymbol{P} = \boldsymbol{T}\bar{\boldsymbol{P}}\boldsymbol{T}^{\dagger} \tag{11}$$

The point of introducing this transformation is to incorporate, via the choice of $\bar{\boldsymbol{P}}$, criteria that will determine the localisation properties of the hybrid basis.

We do this by noting that in the approximation just envisaged a bond $r-s$ formed by overlapping $\bar{\phi}_r$ and $\bar{\phi}_s$ would be described by a bond orbital $a\bar{\phi}_r + b\bar{\phi}_s$. If we assume in the first instance non-polar bonds we have $a = b = \sqrt{1/2}$ and obtain a corresponding charge density contribution (for two electrons and real orbitals)

$$\bar{\phi}_r^2 + \bar{\phi}_s^2 + 2\bar{\phi}_r\bar{\phi}_s .$$

The charge density expression (10) is a sum of such contributions, together with single terms, $2\bar{\phi}_w^2$, representing the lone pairs. This description prescribes the form of $\bar{\boldsymbol{P}}$ in the hybrid basis:

$$\bar{\boldsymbol{P}} = \begin{array}{c|ccccccc|}
 & & r & t & s & u & & w \\
\hline
 & \ddots & & & & & & \\
r & & 1 & & 1 & & & \\
t & & & 1 & & 1 & & \\
s & & 1 & & 1 & & & \\
u & & & 1 & & 1 & & \\
 & & & & & & \ddots & \\
w & & & & & & & 2 \\
\hline
\end{array}$$

– where each array of four 1's refers to a bond, while the diagonal 2's refer to the lone pairs. All other elements are zeros. If no constraints are imposed on the form of $\boldsymbol{T}$ (i.e. if the hybrids can be determined by freely mixing all the AO's) we know that a $\boldsymbol{T}$ exists such that $\boldsymbol{P} = \boldsymbol{T}\bar{\boldsymbol{P}}\boldsymbol{T}^{\dagger}$ and is identical with the matrix found from the AO calculation; for the transformation matrix in (11) is simply the unitary matrix which connects the two bases. In this case the condition

$$E_{\text{orb}} = \operatorname{tr} \boldsymbol{hP} = \operatorname{tr} \boldsymbol{hT\bar{P}T}^{\dagger} = \text{minimum value} \tag{12}$$

must yield values of E_{orb} (and of E) identical with those from the AO calculation. The hybrids found in this way will not necessarily resemble those used in elementary valence theory, for they may contain AO's from *all* atoms in the molecule. If, however, each hybrid turns out to be composed mainly of AO's from a single centre[2], then the elementary description would evidently be a good one; if a hybrid contains AO's from two centres it will indicate a bond with considerable ionic character; while if a hybrid contains AO's from 3 or more centres it will indicate the impossibility of setting up an accurate description of the bond in terms of two-centre bond orbitals. The solutions of (12) will be described as unrestricted hybrids.

The above considerations suggest that the validity of a localised bond description may be assessed by constraining the hybrids, so that the AO's of any atom are mixed only among themselves, and using $\Delta E_{\text{orb}} = E_{\text{orb}}^{(\text{const.})} - E_{\text{orb}}$ as the measure of the error thereby incurred. For we note that the first-order energy error due to an error $\delta \boldsymbol{P}$ in $\boldsymbol{P}$ is given by (6) i.e.

$$\Delta E = \Delta E_{\text{orb}} = \operatorname{tr} \boldsymbol{h}\delta\boldsymbol{P} = \operatorname{tr} \boldsymbol{h}(\boldsymbol{P}^{\text{const.}} - \boldsymbol{P}) = E_{\text{orb}}^{(\text{const.})} - E_{\text{orb}}\,. \tag{13}$$

This constraint is imposed most simply by writing the orbitals sequentially in groups (one group for each atom) and then restricting $\boldsymbol{T}$ to be of block diagonal form, each block determining the hybridisation at a particular centre.

It is also advantageous to consider variations on the particular block form of $\bar{\boldsymbol{P}}$ introduced above, since this form may sometimes be too restrictive. Suppose, for example, that the unrestricted hybrids $\bar{\phi}_r$ and $\bar{\phi}_s$ defining a bond $r-s$ each contain large amounts of the AO's on *both* centres. This indicates that the bond is strongly polar and that the bond orbital $(\bar{\phi}_r + \bar{\phi}_s)/\sqrt{2}$ would not give a good description if only *intra*-atomic AO mixing were allowed. It may, however, be possible to find good constrained hybrids, compatible with the existence of polar bonds, by writing each bond orbital in the more flexible form

$$\cos\theta_{rs}\bar{\phi}_r + \sin\theta_{rs}\bar{\phi}_s\,.$$

Here, $\theta_{rs} = \pi/4$ describes the non-polar situation on which the original specification of $\bar{\boldsymbol{P}}$ is based. The more familiar description in which the hybrids are intra-atomic in character may therefore be retrieved by admitting for each bond a polarity parameter θ_{rs} and taking a more general form for $\bar{\boldsymbol{P}}$:

$$\bar{\boldsymbol{P}} = \begin{array}{c} \\ r \\ s \\ w \end{array} \begin{array}{c} \begin{array}{ccc} r & s & w \end{array} \\ \left[\begin{array}{ccc} P_r & P_{rs} & \\ P_{rs} & P_s & \\ & & 2 \end{array}\right] \end{array} \tag{14}$$

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[2] We note that the AO's "on a single centre" are the orthogonalised AO's formally associated with that centre: regarded as mixtures of the original, non-orthogonal AO's, the hybrids do of course have a certain many-centre character. This should be kept in mind when interpreting the results of calculation.

in which p_r and p_{rs} are the fundamental charge and bond order associated with orbital ϕ_r and bond $r-s$ respectively. In terms of the parameter θ_{rs}

$$p_r = 1 + \cos 2\,\theta_{rs}\,, \qquad p_s = 1 - \cos 2\,\theta_{rs}\,, \qquad p_{rs} = \sin 2\,\theta_{rs}\,. \tag{15}$$

The optimum hybrids of constrained form will be those obtained for the particular choice of θ_{rs} that minimises ΔE and the corresponding wave function will be the best bond orbital ansatz, based on constrained hybrids, with which to approximate the SCF MO function.

Other variations are evidently possible. In some situations, for example, it might be useful to recognise 3-centre bonds; these would be incorporated by adopting a form of $\bar{\boldsymbol{P}}$ corresponding to bond orbitals constructed from three hybrids instead of two. Any assumed bonding scheme merely specifies the form of the matrix $\bar{\boldsymbol{P}}$, and the optimum hybrids which give the best energy compatible with this form are then obtained by solving the variational problem (12), subject to the corresponding constraints, thus obtaining from (13) the smallest possible error. It would, of course, be possible to re-formulate the conventional SCF procedure along similar lines, using the $\boldsymbol{P}$ matrix in calculating the matrix $\boldsymbol{G}$ which appears in the definition of $\boldsymbol{h}$ in (7). At present, however, we are interested mainly in reproducing the results of a given SCF calculation in terms of a function constructed in a simple and chemically appealing way from hybrid orbitals.

3. Method of Solution

There are many ways of achieving the stationary value

$$E_{\text{orb}} = \operatorname{tr} \boldsymbol{h}\boldsymbol{T}\bar{\boldsymbol{P}}\boldsymbol{T}^{\dagger} = \text{minimum value}$$

with the auxiliary condition that $\boldsymbol{T}$ remains a unitary matrix and with any other desired restrictions on the form of this matrix. First, we consider the variation $\boldsymbol{T} \to \boldsymbol{T} + \delta\boldsymbol{T}$ and express the stationary condition in the form

$$\delta E_{\text{orb}} = \operatorname{tr}(\bar{\boldsymbol{P}}\,\delta\boldsymbol{T}^{\dagger}\boldsymbol{h}\boldsymbol{T} + \bar{\boldsymbol{P}}\boldsymbol{T}^{\dagger}\boldsymbol{h}\,\delta\boldsymbol{T}) = 0\,. \tag{16}$$

From the invariance of the trace under cyclic permutation of the matrix product, this may be written $\delta E_{\text{orb}} = \operatorname{tr}\boldsymbol{X}\,\delta\boldsymbol{T}$ and the stationary condition (all $\delta\boldsymbol{T}$) then implies $\boldsymbol{X} = \boldsymbol{O}$. The orthogonality condition $\boldsymbol{T}^{\dagger}\boldsymbol{T} = \boldsymbol{1}$ may be incorporated, introducing Lagrangian multipliers, and leads easily to the final equation

$$\boldsymbol{h}\boldsymbol{T}\bar{\boldsymbol{P}} = \boldsymbol{T}\boldsymbol{\varepsilon} \tag{17}$$

where $\boldsymbol{\varepsilon}$ is a matrix of Lagrangian multipliers which may be chosen to have the hermitian form

$$\boldsymbol{\varepsilon} = \tfrac{1}{2}(\boldsymbol{T}^{\dagger}\boldsymbol{h}\boldsymbol{T}\bar{\boldsymbol{P}} + \bar{\boldsymbol{P}}\boldsymbol{T}^{\dagger}\boldsymbol{h}\boldsymbol{T})\,. \tag{18}$$

There appears to be no simple direct method of solving this matrix equation and it appears to be simpler to minimise E_{orb} directly. This is a purely computational problem leading to a variety of procedures. We could, for example, start from any (unitary) first approximation to $\boldsymbol{T}$ and make successive modifications proportional to the matrix of "residuals" from (17). In this case

$$\delta\boldsymbol{T} = -\lambda(\boldsymbol{h}\boldsymbol{T}\bar{\boldsymbol{P}} - \boldsymbol{T}\boldsymbol{\varepsilon}) \tag{19}$$

where $\boldsymbol{\varepsilon}$ is given in (18) and λ is a numerical parameter. This procedure corresponds to steepest descent of the energy surface and an optimum value of λ may be determined in various ways. If $\boldsymbol{T}$ is constrained to be of block form the same procedure may be followed using partitioned matrices. The optimum correction of the $\boldsymbol{T}$ matrix for atom R is then found to be

$$\delta \boldsymbol{T}^{R} = -\lambda[(\boldsymbol{h}^{RR}\boldsymbol{T}^{R}\overline{\boldsymbol{P}}^{RR} - \boldsymbol{T}^{R}\boldsymbol{\varepsilon}^{RR}) + \sum_{S(\neq R)} (\boldsymbol{h}^{RS}\boldsymbol{T}^{S}\overline{\boldsymbol{P}}^{SR} - \boldsymbol{T}^{R}\boldsymbol{\varepsilon}^{RSR})] \tag{20}$$

where, for example, $\boldsymbol{h}^{RS}$ is the RS-block or sub-matrix of $\boldsymbol{h}$ and

$$\begin{aligned} \boldsymbol{\varepsilon}^{RR} &= \tfrac{1}{2}[(\boldsymbol{T}^{R\dagger}\boldsymbol{h}^{RR}\boldsymbol{T}^{R}\overline{\boldsymbol{P}}^{RR}) + (\text{hermitian conjugate})] \\ \boldsymbol{\varepsilon}^{RSR} &= \tfrac{1}{2}[(\boldsymbol{T}^{R\dagger}\boldsymbol{h}^{RS}\boldsymbol{T}^{S}\overline{\boldsymbol{P}}^{SR}) + (\text{hermitian conjugate})]\,. \end{aligned} \tag{21}$$

In this case the dimensions of the sub-matrices are restricted by the number of orbitals on a single atom and the molecular size is not a limiting factor in the computations. The corrections are made atom-by-atom in a cyclic process until convergence is obtained.

To allow for polarity of the bonds we must minimise E_{orb}, using the block form of $\boldsymbol{T}$ as above, and must also minimise with respect to variation of the polarity parameters, θ_{rs} in equation (15). A straightforward analysis shows that the optimum value of θ_{rs}^{RS}, for a link involving orbitals r, s on atoms R and S respectively is given by

$$\tan 2\theta_{rs}^{RS} = \frac{\bar{h}_{rs}^{RS} + \bar{h}_{sr}^{SR}}{\bar{h}_{rr}^{RR} - \bar{h}_{ss}^{SS}} \quad (\overline{\boldsymbol{h}}^{RS} = \boldsymbol{T}^{R\dagger}\boldsymbol{h}\boldsymbol{T}^{S})\,. \tag{22}$$

The minimising of E_{orb} is conveniently accomplished by starting from the non-polar solution, revising the θ values by (22), correcting each block of the $\boldsymbol{T}$ matrix with the revised θ values, and repeating the process iteratively.

4. Results and Discussion

Detailed calculations have been performed on three molecules (i) methane, (ii) water, and (iii) formaldehyde. In each case, the Hartree-Fock Hamiltonian is taken from a non-empirical SCF calculation based on an orthogonalised set of hybrid AO's. Three approximations are distinguished:

A) A *non-polar* calculation is performed, in which the hybrids are combined in pairs to yield a $\overline{\boldsymbol{P}}$-matrix of the form (14) with $p_r = p_s = p_{rs} = 1$ (for each bond pair) and the *optimum hybrids* are formed from the initially assumed hybrids of each atom, only *intra-atomic* mixing being allowed.

B) Polarisation of the bonds is admitted by iterative revision of the charges and bond orders (via the polarity parameter θ_{rs} in (15)) the calculation being otherwise as in (A).

C) Delocalisation of the optimum hybrids found in (B) is admitted by relaxing the condition that only intra-atomic mixing be permitted. In this case no constraints remain and the results are identical with those of the full SCF calculation.

At each stage of refinement new physical effects are recognised: starting from initial hybrids pointing along the bond directions, (A) allows bond "bending"; (B) allows ionic character to develop, according to the relative electronegativities of the pairs of atoms concerned; and (C) allows delocalisation of the bonding and thus indicates to what extent a "perfect pairing" model is valid. The relative importance of these effects is expected to be widely different in the three molecules considered; in methane the hybrids are largely determined by symmetry, there can be no bending and the interesting features are the bond polarity and degree of delocalisation; in water the hybrids may be set up by the simple prescription of pointing them along the bond directions (lone pairs being determined by orthogonality conditions), but the lower symmetry allows the development of some degree of bending; in formaldehyde the corresponding prescription leaves the *oxygen* hybrids undetermined, and the nature of the valence state is an open question.

The results of these calculations are embodied in Tables 1–3, and will be discussed briefly, molecule by molecule.

(i) *Methane*. The initial hybrids are set up by symmetrically orthogonalising [18] the usual set of tetrahedral sp^3 hybrids. The integrals and the Hartree-Fock Hamiltonian on this basis are available from the work of Klessinger and McWeeny [15]. The results are shown in Table 1. For this molecule the optimum hybrids in approximations A and B are identical with the initial hybrids, as would be expected from symmetry considerations. When polarisation is admitted, the energy error falls virtually to zero. When further delocalisation of the hybrids is allowed

Table 1. *Results for CH_4*

Approximation[a]	*Populations and bond orders*			*Energy error (a.u.)*
	b_1	h_1	$b_1 - h_1$	
A	1.0	1.0	1.0	0.063
B	1.080	0.920	0.997	0.000

Optimum hybrids

A, B	$b'_1 = b_1$
C	$b'_1 = 0.999\, b_1 - 0.042\, h_1 + 0.012\,(h_2 + h_3 + h_4)$

$b_1, \ldots, b_4$ are bond hybrids pointing towards hydrogen AO's $h_1, \ldots, h_4$.

[a] Approximations A, B, C are described in the text. The populations and bond orders in C coincide with those in B.

Table 2. *Results for H_2O*

Approximation[a]	*Populations and bond orders*			*Energy error (a.u.)*
	b_1	h_1	$b_1 - h_1$	
A	1.0	1.0	1.0	0.020
B	1.117	0.883	0.993	0.002

Optimum hybrids

A	$b'_1 = 0.998\, b_1 - 0.002\, b_2 - 0.046\,(l_1 + l_2)$ $l'_1 = 0.998\, l_1 - 0.002\, l_2 + 0.046\,(b_1 + b_2)$
B	$b'_1 = 0.999\, b_1 - 0.001\, b_2 - 0.031\,(l_1 + l_2)$ $l'_1 = 0.999\, l_1 - 0.001\, l_2 + 0.031\,(b_1 + b_2)$
C	$b'_1 = 0.999\, b_1 - 0.012\,(l_1 + l_2) - 0.012\, h_2 + \cdots$ $l'_1 = 0.999\, l_1 + 0.012\,(b_1 + b_2) - 0.012\,(h_1 + h_2) + \cdots$

b_1, b_2 are bond hybrids pointing towards hydrogen AO's h_1, h_2; l_1, l_2 are lone pair hybrids (completing a roughly tetrahedral set). In approximation C, terms with coefficients less than .005 have been omitted.

[a] Approximations A, B, C are described in the text. The populations and bond orders in C coincide with those in B.

Table 3. *Results for CH_2O*

Approximation[a]	*Populations and bond orders*									*Energy*
	b_1	h_1	b_1-h_1	σ_C	σ_O	$\sigma_C-\sigma_O$	π_C	π_O	$\pi_C-\pi_O$	*error (a.u.)*
A	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.130
B	1.107	0.893	0.994	0.880	1.120	0.993	1.032	0.968	1.000	0.101

	Optimum hybrids
A	$b'_1 = 0.999\, b_1 + 0.028\, \sigma_C$ $\sigma'_C = 0.999\, \sigma_C - 0.028\, (b_1 + b_2)$ $\sigma'_O = 0.999\, \sigma_O - 0.037\, (l_1 + l_2)$ $l'_1 = 0.999\, l_1 + 0.037\, \sigma_O - .001\, l_2$
B	$b'_1 = 0.999\, b_1 + 0.038\, \sigma_C - 0.001\, b_2$ $\sigma'_C = 0.999\, \sigma_C - 0.038\, (b_1 + b_2)$ $\sigma'_O = 0.999\, \sigma_O - 0.024\, (l_1 + l_2)$ $l'_1 = 0.999\, l_1 + 0.024\, \sigma_O$
C	$b_1 = 0.995\, b_1 + 0.019\, \sigma_C - 0.059\, l_1 + 0.072\, l_2 + 0.015\, h_1 + 0.020\, h_2 - 0.007\, \sigma_0 + \cdots$ $\sigma'_C = 0.999\, \sigma_C + 0.019\, (b_1 + b_2) + 0.012\, (l_1 + l_2) - 0.007\, (h_1 + h_2) + \cdots$ $\sigma'_O = 0.999\, \sigma_O - 0.011\, (l_1 + l_2) + 0.017\, (h_1 + h_2) + 0.007\, (b_1 + b_2) + \cdots$ $l'_1 = 0.990\, l_1 + 0.010\, \sigma_O + 0.061\, b_1 - 0.074\, b_2 - 0.066\, h_1 + 0.081\, h_2 - 0.012\, \sigma_C + 0.010\, l_2 + \cdots$

$b_1 b_2$ are carbon bond hybrids pointing towards hydrogen AO's h_1, h_2; σ_C is the carbon C–O bond hybrid; $l_1 l_2$ are oxygen (sp^2) lone pair hybrids; σ_O is the oxygen C–O bond hybrid; π_C and π_O are carbon and oxygen AO's of the π bond. All σ orbitals are coplanar, l_i and b_i, h_i being on the same side of the C–O bond. In approximation C terms with coefficients less than .005 have been omitted.

[a] Approximations A, B, C, are described in the text. The populations and bond orders in C coincide with those in B.

(approximation C) the energy is in exact agreement with that from the SCF calculation; this delocalisation is clearly slight and not significant energetically.

(ii) *Water.* The initial hybrids are constructed by orthogonalising the roughly tetrahedral set in which two hybrids point along the bond directions and the other two hold the lone pairs. The SCF data were obtained from calculations by Klessinger [19]. The results appear in Table 2. With the assumption of non-polar bonds the energy is in error by .020 a.u., but this is reduced to .002 a.u. when polarisation is allowed. In both cases the optimum hybrids are very close to the initial hybrids, indicating an insignificant amount of "bond bending." On allowing further delocalisation (approximation C) the error of .002 a.u. is eliminated, but the hybrids themselves are still not seriously affected.

(iii) *Formaldehyde.* The initial hybrids were those employed by Cook, Hollis and McWeeny [16] in approximate ab initio calculations, the oxygen valence state being assumed trigonal in anticipation of the expected high localisation of the final lone pair orbitals. The accurate SCF calculations were based on integrals obtained by Newton [20]. The results in Table 3 indicate that the first approximation (A) is in this case much poorer, giving an energy error of 0.130 a.u. This error is reduced by only 0.029 a.u. by admitting bond polarisation and the residual 0.101 a.u. is connected wholly with delocalisation effects. First, however, we note that the polarities of the C–O σ and π bonds are in opposition; 0.120 of a σ electron is donated by the carbon to the oxygen, but this represents an over-compensation for the greater electronegativity of the oxygen, and there is consequently a *back*-donation of 0.032 of a π electron. Such an effect is widely recognised in the study of inorganic complexes, but is in conflict with the assumptions usually made in organic chemistry, where nitrogen and oxygen are normally assumed to have a *greater* affinity, *even for π electrons*, than carbon. The origin of the second important feature of these results, namely the considerable delocalisation energy, is evident from a study of the optimum hybrids in Approximation C (which exactly reproduce the SCF results). All the orbitals of the localised bonds are, in fact, contaminated to a considerable degree by admixture of the initially adopted lone pair orbitals. In other words a substantial part of the σ bonding arises from delocalised orbitals which spread all the way from the hydrogen atoms to the oxygen lone pair region. This result is in contrast with that obtained for methane, where there are no lone pairs and where mixing of different hybrids is precluded by symmetry considerations.

It is not the intention, in this paper, to present a more detailed analysis of the charge distribution in the molecules considered. It is clear, however, that the localisation procedure here adopted allows us to give a quantitatively significant analysis of hitherto ill-defined effects such as bond bending, bond polarisation and bond delocalisation, and to discuss the importance of these effects in terms of energy contributions. More detailed discussion of the charge density itself, and of the use of optimum hybrids in CI calculations, will be taken up in later papers.

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References

1. Lennard-Jones, J. E.: Proc. Roy. Soc. (Lond.) A **198**, 14 (1949) and subsequent papers in the same series. See also: Coulson, C. A., Trans. Farad. Soc. **33**, 388 (1937) where the bond orbital concept seems first to have been introduced.
2. Murrell, J. N.: J. chem. Physics **32**, 767 (1960).
3. Gilbert, T. L., and P. G. Lykos: J. chem. Physics **33**, 2199 (1962).
4. Golebiewoki, A.: Trans. Faraday Soc. **57**, 1849 (1961).
5. Coulson, C. A., and H. Goodwin: J. chem. Soc. (London) 2851, 1962.
6. Del Re, G.: Theoret. Chim. Acta (Berl.) **1**, 188 (1963).
7. Veillard, A., and Del Re, G.: Theoret. Chim. Acta (Berl.) **2**, 55 (1964).
8. Certain, P. R., V. S. Watts, and J. H. Goldstein: Theoret. Chim. Acta (Berl.) **2**, 324 (1964).
9. Edmiston, C., and K. Ruedenberg: Rev. Mod. Physics **35**, 457 (1963).
10. Del Re, G., U. Esposito, and M. Carpentieri: Theoret. Chim. Acta (Berl.) **6**, 36 (1966).
11. Magnasco, V., and A. Perico: J. chem. Physics **47**, 971 (1967).
12. McWeeny, R., and K. Ohno: Proc. Roy. Soc. (London) A **255**, 367 (1960).
13. Grahn, R.: Arkiv for Fys. **21**, 1 (1968).
14. Tsuchida, A., and K. Ohno: J. chem. Physics **39**, 600 (1963).
15. Klessinger, M., and R. McWeeny: J. chem. Physics **42**, 3343 (1965).
16. Cook, D. B., P. C. Hollis, and R. McWeeny: Molecular Physics (in the press).
17. Carlson, B. C., and J. M. Keller: Physic. Rev. **105**, 102 (1957).
18. Lowdin, P.-O.: J. chem. Physics **18**, 365 (1950).
19. Klessinger, M.: J. chem. Physics **43**, S 117 (1965).
20. Newton, M. D., and W. E. Palke: J. chem. Physics **45**, 2329 (1966).

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