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Electron Distribution and Chemical Binding

J. L. J. ROSENFELD*

Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden

The electron distribution in a series of bond types and molecules is analysed using the Roux δ function. For σ bonds and lone pair orbitals distinct regions of positive δ are found localised where classically the bond or lone pair would be drawn. It is shown that for a given bond there is a good correlation between the bond strength calculated by an approximate wave function and the maximum value of δ in the bonding region obtained from the same function. It is suggested that a better correlation might be found by integrating the δ function over the region in space where it is positive.

I. INTRODUCTION

It has long been realised that the formation of a molecule from a number of atoms is intimately connected with a change in the electron distribution among them, as a result of which the total energy of the system is lowered.[1] It is also well known that the binding energy is only a small fraction (generally about $\frac{1}{2}$ %) of the total electronic energy. Because of this one can consider the formation of a molecule as being the result of a small perturbation on the atoms concerned. One may therefore expect that the change in the electron distribution on formation of a molecule will also be small, and one might hope that such changes would by and large be restricted to those regions where the interaction was strongest, that is in the regions between those atoms where the traditional "chemical bonds" are supposed to be localised. The recent trend in the increased complexity of molecular wave functions, based on essentially delocalised one electron functions (*e. g.* the Molecular Orbital methods) has made it rather difficult to obtain simple correlations between them and the idea of localised bonds. Such correlations are extremely desirable, since the concept of a chemical bond is so well established and has proved so successful in explaining and correlating all kinds of experimental data. Looking at a complicated wave function is not generally as illuminating as looking at a structural formula. Two such correlations have been introduced in the past decade. The first, Mulliken's population analysis,[2] divides the electron distri-

* Present address. Department of Chemistry, Brown University, Providence, Rhode Island, U.S.A.

bution into two parts, the net atomic populations and the overlap populations. Bonding, bond order and bond strengths are correlated with the overlap population. In another analysis the whole electron distribution is divided up among the atoms to yield the gross atomic populations. These quantities are correlated with charge transfer (hence with the dipole moment), with hybridisation and with electron affinities. This method has become widely accepted and most publications dealing with LCAO MO wave functions include such an analysis. It has the advantage of being able to deal with one molecular orbital or one atomic orbital at a time, thus pinpointing those responsible for bonding, *etc.*; but has the disadvantage that, since the quantities it deals with are electron distributions integrated over the whole of space, detail is lost, in particular with regard to the precise localisation of a bond. Furthermore, since it does not seek to compare in a quantitative manner a molecule and a similar (hypothetical) noninteracting system of atoms, it is difficult to understand, on a quantitative basis, exactly what changes have occurred as a result of the interatomic interactions (for example there may be a large overlap population between two noninteracting atoms placed hypothetically in the positions they occupy in the molecule considered).

The second attempt to find connections between the complex molecular wave functions and the localised chemical bonds was introduced in 1956 by Roux and collaborators.[3-7] In this method the electron density of the molecule is compared directly with the hypothetical distribution which would be obtained if the atoms occupied the same positions as in the molecule, but without interacting. In general also, the electron distribution for each atom is made spherically symmetrical (*e.g.* for the four electrons in the (2*p*) shell of the oxygen atom), since any polarisation or fixing of the axes of the atoms in space implies some interaction. As will be seen later there are special cases when the assumption of the fixing of at least one axis in space gives further insight into the connection between the chemical bond and the difference (called δ) between the two electron distributions discussed above. In contrast to the calculation of overlap and atomic populations, which are easily done on a desk calculator, the calculation of the δ function is generally laborious and is only feasible for a large number of molecules if an electronic computer is used. Furthermore it is not generally useful to consider any one molecular orbital in isolation, though it is feasible to consider orbitals of a given symmetry as a group.

Recently, Shull [8,9] has analysed two-electron bonds in terms of atomic and ionic character. For homonuclear molecules he shows, starting from an expansion of the wave function in terms of natural orbitals, that both the atomic and ionic parts of a wave function are non-bonding, whereas it is the cross term which is strongly bonding and can be related to the concept of "covalency". For heteronuclear molecules he also obtains a parameter which correlates well with the electronegativity difference between the atoms. This method is also absolute in the sense that no comparison is made between the molecule and its constituent atoms. This method is apparently restricted at present to diatomic molecules.

It is the Roux δ function which is discussed in greater detail in the remainder of this paper.

Consider a system of N electrons represented by the normalised wave function Ψ. The electron density ϱ at a point p can be written (in atomic units*)

$$\varrho_p = \sum_{m=1}^{N} \left[\int\int \Psi^* \Psi \frac{d\tau}{d\tau_m} d\sigma \right]_{\tau_m = p} \tag{1}$$

where $\int....d\sigma$ means summation over all the spins and $\int....d\tau/d\tau_m$ means integration over the space coordinates of all but the mth electron. The coordinates τ_m of this electron take the value p.

When Ψ is some linear combination of M ($M>N$) one-electron functions (*e.g.* atomic orbitals), it is possible,[6,10] to rewrite eqn. (1) and obtain

$$\varrho_P = \left[\sum_{m=1}^{M} \sum_{n=1}^{M} c_{mn} \chi_m^* \chi_n \right]_P \tag{2}$$

where the χ_m are the one electron functions of the space coordinates (r,θ,φ). The matrix $\mathbf{C}$ whose elements are c_{mn} is known as the density matrix.

For the system of non-interacting atoms, the density ϱ^F is obtained by a superposition of the atomic electron density fucntions, averaged over the angular coordinates of the electrons. Each atomic orbital is assumed to be a product of a radial and an angular function:

$$\chi_n = R_m(r) Y_m(\theta,\varphi) \tag{3}$$

For the product $\chi_m^* \chi_n$, the averaging yields

$$\overline{\chi_m^* \chi_n} = R_m^* R_n \frac{\int\int Y_m^* Y_n \sin\theta \, d\theta \, d\varphi}{\int\int \sin\theta \, d\theta \, d\varphi} = R_m R_n \overline{Y_m^* Y_n} \tag{4}$$

Thus ϱ^F is obtained as

$$\varrho^F = \sum a_{mn} R_m R_n \overline{Y_m^* Y_n} \tag{5}$$

where a_{mn} is analogous to c_{mn} in eqn. (2). The δ function is simply the difference between ϱ and ϱ^F,

$$\delta = \varrho - \varrho^F = \sum_{m,n} (c_{mn} \chi_m^* \chi_n - a_{mn} R_m R_n \overline{Y_m^* Y_n}) \tag{6}$$

Note that the orbitals used for the molecular wave function are not necessarily the same as those for the atomic functions.

II. TWO-ELECTRON BONDS

In order to gain insight into the connection between the δ function and the concept of the chemical bond, it is easier to consider a single doubly-filled molecular orbital ψ in a diatomic molecule AB. To calculate ϱ^F, we assume there is one electron on each atom A and B, whose wave functions are χ_A and χ_B respectively. Several expansions for ψ can be considered. In the simplest

* One a.u. of length = the Bohr radius, one a.u. of charge = the electronic charge. These are obtained by letting $h = e = m_e = c = 1$.

case (case I) ψ is a linear combination of the same two orbitals χ_A and χ_B. In a better approximation (case II), ψ is a linear combination of two orbitals Φ_A and Φ_B which differ from χ_A and χ_B in the value of the exponent. In either case we can write

$$\chi(r,\theta,\varphi) = F(r)\cdot\Phi(r,\theta,\varphi) \tag{7}$$

where for normalised Slater-type orbitals of principal quantum number n,

$$F(r) = \gamma^{(2n+1)/2}\exp[(1-\gamma)\alpha r] \tag{8}$$

in which $\gamma = \beta/\alpha$ is the ratio of the exponents in χ (β) and Φ (α), respectively. The angular functions of χ and Φ are identical. In case I, γ and hence F take the value 1.

Finally, ψ may be a linear combination of more than two atomic orbitals. This approximation is not considered here because it is in a sense equivalent to case II. It was used however in obtaining the functions in a series of molecules as described in the last section of the paper.

We can now obtain δ by noting that

$$\psi = c_A\Phi_A + c_B\Phi_B \tag{9}$$

and that since ψ, Φ_A and Φ_B are all assumed normalised,

$$c_A^2 + c_B^2 + 2c_Ac_BS = 1, \tag{10}$$

where $S = \langle\Phi_A|\Phi_B\rangle$ is the overlap integral. Substituting into eqn. (6) from eqns. (3), (4), (8), (9) and (10) yields

$$\delta = \frac{(2c_A^2-1)(S\Phi_A^2-\Phi_A\Phi_B)+(2c_B^2-1)(S\Phi_B^2-\Phi_A\Phi_B)}{S}$$
$$+ R_A^2(Y_AY^*_A - F_A^2\overline{Y_A^*Y_A}) + R_B^2(Y_B^*Y_B - F_B^2\overline{Y_B^*Y_B}) \tag{11}$$

Here, I have for convenience written Φ^2 instead of $\Phi^*\Phi$ and $2\Phi_A\Phi_B$ instead of $(\Phi_A^*\Phi_B + \Phi_B^*\Phi_A)$.

The effect of F_A and F_B can now be gauged. From eqn. (8) it is clear that if $\gamma < 1$, then F is smallest at small r, and *vice versa*. Thus one expects δ (case I) to be less than δ (II) near those atoms for which $\gamma < 1$, and *vice versa*. This is illustrated in Fig. 1, which shows δ functions along the internuclear axis

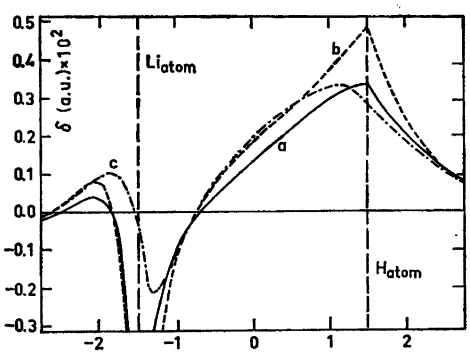


Fig. 1. LiH molecule. δ along the internuclear axis. Calculated using Ransil's SCF functions.[11] a) Slater exponents in both molecular and atomic wave functions. b) "Best limited" exponents in both molecular and atomic wave functions. c) "Best limited" and "best atom", respectively, in molecular and atomic wave functions.

for LiH, calculated with different wave functions all taken from Ransil's paper.[11] Curve *a* was obtained using Slater exponents both for the molecular and atomic wave functions. For Curve *b* again the exponents for both density functions were the same but this time Ransil's "best limited" values were used. In calculating curve *c* the "best limited" set was used for the molecular wave function, and the "best atom" values for the atoms. Curves *a* and *b* therefore represent case I ($\gamma = 1$), whereas curve *c* represents case II. In this instance $\gamma < 1$ for Li and $\gamma > 1$ for H. It is clearly seen that δ (curve *c*) is largest of the three near the Li atom, and smallest near the H atom. Curves *b* and *c* are the more nearly comparable since they were both obtained with the same molecular wave function so that the differences between them are entirely due to the different values of γ. A similar effect has been observed for C_2 and C_4.[12]

When $F = 1$ (case I), several interesting conclusions may be drawn from eqn. (11). Firstly, for *s* orbitals the last two terms vanish, whereas for other orbitals they are in general non-zero. For example, for p_z functions ($Y^*Y - \overline{Y^*Y}$) $\propto (3\cos^2\theta - 1)$. Secondly, from eqn. (10) it follows (for $S > 0$, which is usually the case) that if $(2c_A^2 - 1)$ is positive, then $(2c_B^2 - 1)$ will necessarily be negative and *vice versa*. Hence for a polar bond, with A electronegative relative to B, ($c_A > c_B$), δ will be largest (and positive) where Φ_A is largest, and smallest (and negative) where Φ_B is largest. For a $2p\sigma$ bond, the last two terms will contribute positively to δ when θ_A and θ_B are small (the *z* axes being defined as pointing toward each other), so that δ will be greatest along the internuclear axis. Thus we are led to expect a region of positive δ between the nuclei, closer to the more electronegative atom (*cf.* Ref.[1], p. 107 ff. and also Fig. 1). A further interesting conclusion may be drawn when F is not equal to 1, namely that, for sufficiently large r, δ will always become negative if $\gamma < 1$ for those orbitals which contribute most to δ in that region. Hence in case II, the positive regions of δ are closed if $\gamma < 1$. Examination of γ for a series of molecules (see Ref.[11]) shows that in fact $\gamma < 1$ for the outlying valence orbitals when the exponents are optimised separately (with respect to the energy) for the atoms and molecules. Similar closed regions of positive δ values are obtained if ψ is improved over case I by enlarging the basis set in the molecular wave functions (with or without changing the exponents). It seems probable therefore that these closed regions are a real phenomenon and that they may be associated with localised changes in electron density on bond formation. They do not necessarily occur if ψ is given by case I.

For a more quantitative analysis we consider next the simpler case of homonuclear molecules. For these, $c_A = c_B$ and hence eqn. (10) gives

$$(2c_A^2 - 1) = (2c_B^2 - 1) = -S/(1+S) \tag{12}$$

so that eqn. (11) becomes

$$\delta = \frac{1}{(1+S)}\left[2\Phi_A\Phi_B - S(\Phi_A^2 + \Phi_B^2)\right] + R_A^2(Y_A^*Y_A - F_A^2\overline{Y_A^*Y_A}) + R_B^2(Y_B^*Y_B - F_B^2\overline{Y_B^*Y_B}) \tag{13}$$

(i) The 1*s*-1*s* bond: The hydrogen molecule

For this molecule,

$$\Phi_A = \left[\frac{\alpha^3}{\pi}\right]^{\frac{1}{2}} \exp(-\alpha r_A) \ , \ Y_A^* Y_A = \overline{Y_A^* Y_A} = 1 \tag{14}$$

$$F_A^2 = \gamma^3 \exp[2(1-\gamma)\alpha r_A] \ , \ \gamma = 1/\alpha$$

since for the H atom $\beta = 1$.

Similar expressions hold for Φ_B, $Y_B^* Y_B$ and F_B^2. The expression for δ takes on a simpler form if the unit of length is rescaled by a factor α. This is accomplished by the following substitions:

$$\alpha r_A = R_A \ , \ \alpha r_B = R_B \ , \ R_A + R_B = R \ , \ \alpha r_{AB} = R_0 \ , \ \Delta = \delta/\alpha^3 \tag{15}$$

Eqn. (13) then becomes

$$\begin{aligned} \Delta = & \frac{1}{\pi(1+S)} \left\{ 2\exp(-R) - S\left[\exp(-2R+2R_A) + \exp(-2R_A)\right] \right\} \\ & + \frac{\exp(-2R_A)}{\pi}\left[1-F_A^2\right] + \frac{\exp(-2R+2R_A)}{\pi}\left[1-F_B^2\right] \end{aligned} \tag{16}$$

From this equation it is clear that Δ reaches a maximum for arbitrary R when $R_A = R_B = \frac{1}{2}R$, *i.e.* along the perpendicular bisector of the internuclear axis. Along this line $\Delta = \Delta_m$, say, where

$$\Delta_m = \frac{2\exp(-R)}{\pi}\left[\frac{1-S}{1+S} + (1-F^2)\right] \tag{17}$$

in which $F_A^2 = F_B^2 = F^2$, since $R_A = R_B$ along the line considered.

Δ_m in turn is greatest when R is smallest, that is when $R = R_0$, at the center of the molecule. At that point $\Delta = \Delta_c$. Since S is a function of R_0 only,[13] in this case

$$S = [1 + R_0 + (R_0^2/3)]\exp(-R_0) \tag{18}$$

it then follows from eqns. (17) and (14) that Δ_c is a function of R_0 and α only. When $\alpha = 1$ ($\gamma = 1$, case I), Δ_c is a function of R_0 which has a single maximum at $R_0 = 1.72$. Unfortunately this interesting property disappears for any constant value of $\alpha > 1$ (case II, $\gamma < 1$). Coulson [14] optimised the energy by varying only the internuclear distance, keeping $\alpha = 1$. He obtained the maximum binding energy at $R_0 = 1.61$. In another calculation [14] he varied both r_{AB} and α, and obtained a maximum at $\alpha = 1.197$, $r_{AB} = 1.3833$, *i.e.* at $R_0 = 1.66$, $\gamma = 0.835$. The first calculation corresponds to case I, the second to case II. The values of δ_c and the binding energy D, are shown in Table 1 for these and for the Heitler-London and James-Coolidge (5 term) functions (Ref.[3], p. 939, Figs. 1, 2; for these latter functions δ is not obtained from eqn. (13), since ψ is not given by eqn. (9)). There is a good correlation between δ_c and D, except for the worst function. It is probable that this correlation reflects the physically more reasonable one between D and the total build up of charge between the atoms. This latter quantity would best be represented by the integral of δ over all positive values. It may be that δ_c no longer reflects the

value of this integral for the worst wave function. Such an integration is similar but not equivalent to Mulliken's analysis,[2] in which one integrates over the whole of space, instead of over a localised region as is suggested here (see Ref.[3], p. 939 for a further discussion).

At one of the nuclei, B say, $R_A = R_0$, $R_B = 0$, and from eqn. (16) and (14) Δ_n is obtained as

$$\Delta_n = \frac{2\exp(-R_0) - S(\exp(-2R_0)+1)}{\pi(1+S)} + \frac{\exp(-2R_0)}{\pi}\left[1-\gamma^3\exp(1-\gamma)R_0\right] + \frac{1-\gamma^3}{\pi} \tag{19}$$

For $\gamma = 1$, Δ_n is negative for all values of R_0 (except $R_0 = 0$, $\Delta_n = 0$), but when $\gamma > 1$, Δ_n may be positive. Indeed, for the Coulson (case II) function mentioned above, as for the James-Coolidge function, Δ_n is positive. For the Coulson (case I) and the Heitler-London functions, Δ_n is negative. This may be a further indication of how good a wave function has to be before δ calculated from it has the same qualitative properties as the γ function obtained with an accurate wave function.

Table 1. δ_c and the binding energy D for H_2.

Function	δ_c (a.u.)	D (e.v.)	R_0	γ	r_{AB} (a.u.)
Coulson (case I)	0.023	2.68	1.61	1.0	1.61
Heitler-London	0.021	3.14	1.51	1.0	1.51
Coulson (case II)	0.0883	3.47	1.66	0.835	1.383
James-Coolidge (5 term)	0.105	4.50	–	–	1.40
Experimental	–	4.72	–	–	1.41

(ii) The 2*s*-2*s* bond: The lithium molecule

Here

$$\Phi_A = \left[\frac{b^5}{\pi}\right]^{\frac{1}{2}} N(r_A - a)\exp(br_A),\quad Y_A^* Y_A = \overline{Y_A^* Y_A} = 1 \tag{20a}$$

in which the normalisation constant N is

$$N = [2(3-3ab+2a^2b^2)]^{-\frac{1}{2}} \tag{20b}$$

Similar expression hold for Φ_B. If the parameters are b', a' and N' for the atomic wave functions then F_A is obtained from eqn. (8) as

$$F_A^2 = \gamma^5\left(\frac{N'}{N}\right)^2\left[\frac{r_A - a'}{r_A - a}\right]^2 \exp 2(1-\gamma)br_A \text{ with } \gamma = b'/b \tag{21}$$

When the unit of length is rescaled in equations analogous to eqn. (15), the Δ function is obtained by the substitution of eqns. (20) and (21) into eqn. (13). It is again found that for arbitrary R, Δ reaches a maximum along the perpendicular bisector of the internuclear axis. In this case, the equation analogous to eqn. (17) is

$$\Delta_m = \frac{N^2}{2\pi}(R-ab)^2 \exp(-R)\left[\frac{1-S}{1+S} + (-F^2)\right] \tag{22}$$

Because of the factor $(R-ab)^2$, Δ_m now reaches a maximum at

$$R = 2(1+ab) \text{ or } R = R_0 \tag{23}$$

whichever is the larger. Thus for $R_0 < 2(1+ab)$, the $2s$-$2s$ bond displays a ring of maximum δ values around the centre. However, this situation does not occur for the Li_2 molecule in its ground state. Coulson and Duncanson [15] have treated Li_2 as a two-electron problem using the wave function discussed here. At an internuclear distance $r_{AB} = 5.0$ a.u., they obtain the best energy when $a = 1.000$, $b = 0.81$, which values correspond to $R_0 = 4.05$ and $2(1+ab) = 3.63$. For the Li atom they obtain the optimum parameters as $a' = 0.867$, $b' = 0.767$ or $\gamma = 0.947$, $N'/N = 0.9985$.

An analysis of Δ_c as a function of R_0 again shows a single maximum (at $R_0 = 4.05$) when it is assumed that $\gamma = 1$, but as for the $1s$-$1s$ bond this feature disappears when the wave function is improved by setting $\gamma < 1$. At the nuclei, Δ_c is negative for this function for $\gamma < 1$, but for more accurate wave functions (including the $1s$ electrons and an extended basis set), δ is found to be positive at the nuclei.[4]

Table 2 shows δ_c and the binding energy D calculated with the Coulson-Duncanson function, several SCF functions, and the function including configuration interaction (C.I.). Except for Ransil's function,[11] the values of δ_c have been taken from Fig. 2 in Ref.[4] There is some inconsistency among the SCF functions,* so that the trend in δ_c is somewhat uncertain. There does seem to be a correlation in this case also between δ_c and D except for the C. I. function. Roux has pointed out [4] that this function includes π-π interactions for which δ has a minimum at the centre of the molecule (see later). For this function however the region of positive δ values extends further off the internuclear axis (see Figs. 3, 3' in Ref.[4]), so that the integral of δ over this positive region may still be largest for this function. Another feature of Tables 1 and 2 is that both δ_c and D are about ten times smaller for Li_2 than for H_2. This suggests that the correlation between them is independent of the molecule considered, within the class considered here, namely homonuclear diatomic molecules with σ bonds.

* For an SCF LCAO MO function using $1s$, $2s$ and $2p\sigma$ atomic orbitals on each Li atom as a basis set, Ransil's "best limited" exponents [11] should yield the lowest energy. Faulkner's function used in Ref.[4] however, reportedly gives an even better energy. Dr. Ransil in a private communication expresses his opinion that this discrepancy is due to inaccuracies in the values particularly of certain hybrid integrals used by Faulkner. Because of these the third decimal in Faulkner's result is not reliable. Any consequent errors in the coefficients could, of course, result in erroneous δ values.

Table 2. δ_c and the binding energy D for Li_2.

Function	δ_c	D	R_0	γ	r_{AB}	Basis set for MO
Coulson-Duncanson	0.002	−0.30	4.05	0.947	5.0	2*s*
Ransil SCF (Slater)	0.006	0.15	3.28	1.0	5.05	1*s*, 2*s*, 2*pσ*
Faulkner's incomplete SCF[1a]	0.008	0.22	3.23	1.0	5.05	1*s*, 2*s*
Faulkner's Complete SCF[a]	0.008	0.33	3.23	1.0	5.05	1*s*, 2*s*, 2*pσ*
Kotani *et al.* 4 configurations[a]	0.005	0.732	—	1.0	5.0	includes *π*-*π* configuration
Experimental		1.05	—	—	5.05	

[a] See Ref.[3,4] for details and other references. For Faulkner's function see also footnote on p. 1726.

(iii) The $2p\sigma$-$2p\sigma$ bond

There is no molecule which corresponds to this bond in isolation, B_2 is the nearest to it, but the bond there is partly 2*s*-2*s* is nature (see the coefficients of the SCF LCAO MO wave function,[16] which yield an *s*-*p* hybridisation 22, 33 and 47 % for $R_0 = 4.5$, 4.0 and 3.5, respectively). It is, however, of interest, since the angular function is no longer constant. For this bond,

$$\Phi_A = \left[\frac{\alpha^5}{\pi}\right]^{\frac{1}{2}} r_A \cos\theta_A \exp(-\alpha r_A),\ Y_A^* Y_A = \cos^2\theta_A,\ \overline{Y_A^* Y_A} = \tfrac{1}{3} \tag{24}$$

with similar expressions for Φ_B *etc.* The *z* axes are defined as pointing toward each other, so that eqn. (9) may represent a bonding orbital. In terms of the scaled unit of length eqn. (13) becomes

$$\Delta = \frac{2R_A R_B \cos\theta_A \cos\theta_B \exp(-R) - S[R_A^2 \cos^2\theta_A \exp(-2R_A) + R_B^2 \cos^2\theta_B \exp(-2R_B)]}{\pi(1+S)}$$
$$+ \frac{R_A^2 \exp(-2R_A)}{\pi}\left[\cos^2\theta_A - \frac{F_A^2}{3}\right] + \frac{R_B^2 \exp(-2R_B)}{\pi}\left[\cos^2\theta_B - \frac{F_B^2}{3}\right] \tag{25}$$

where F_A^2 is given by eqn. (8) as

$$F_A^2 = \gamma^5 \exp\ 2(1-\gamma)R_A \tag{26}$$

For arbitrary R, Δ again reaches a maximum along the line $R_A = R_B = \frac{1}{2}R$. Along this line

$$\cos\theta_A = \cos\theta_B = R_0/R \tag{27}$$

so that Δ_m is obtained from eqn. (25) as

$$\Delta_m = \frac{R_0^2 \exp(-R)}{2\pi(1+S)}\left[\frac{1-S}{1+S} + 1 - \frac{R^2 F_A^2}{3R_0^2}\right] \tag{28}$$

This is clearly a maximum when R is as small as possible, *i.e.* when $R = R_0$, at the centre of the molecule. A new feature arises, however, in that Δ_m becomes negative even when $\gamma = 1$, when

$$R^2 F_A^2 = 6R_0^2/(1+S)$$

Furthermore, Δ_m reaches a minimum for $\gamma = 1$ at

$$R = 1 + \left[1 + \frac{6R_0^2}{1+S}\right]^{\frac{1}{2}} \tag{29}$$

and at some other large value of R when $\gamma < 1$. At the centre,

$$\Delta_c = \frac{R_0^2 \exp(-R_0)}{6\pi(1+S)}\left[6 - F^2(1+S)\right] \tag{30}$$

which is positive when $\gamma \leq 1$ for all values of R_0 of interest physically. At the nuclei (say atom B)

$$\Delta_n = \frac{R_0^2 \exp(-2R_0)}{3\pi(1+S)}\left[3 - F_A^2(1+S)\right] \tag{31}$$

which is positive when $\gamma \leq 1$. However, beyond the nuclei, $\cos\theta_B$ changes sign so that the first term in eqn. (25) becomes negative, and Δ will also become negative at some finite R. Thus, in contrast to the s-s bonds, the $2p\sigma$-$2p\sigma$ bond displays a closed region of positive δ values even when $\gamma = 1$ (case I), and this region encompasses the nuclei and the space between them close to the internuclear axis.

(iv) The $2p\pi$-$2p\pi$ bond

Here

$$\Phi_A = \left[\frac{\alpha^5}{\pi}\right]^{\frac{1}{2}} r_A \frac{\sin\theta_A}{2} \exp(i\varphi_A - \alpha r_A)$$

$$Y_A^* Y_A = \frac{\sin^2\theta_A}{2}, \quad \overline{Y_A^* Y_A} = \tfrac{1}{3} \tag{32}$$

and similarly for B. The axes are so defined that the angles φ_A and φ_B are equal. Δ is therefore given by eqn. (25), provided $\cos^2\theta$ is replaced by $(\sin^2\theta)/2$. Along the line $R_A = R_B$,

$$\sin^2\theta_A = \sin^2\theta_B = (R^2 - R_0^2)/R_0^2 \tag{33}$$

and therefore the following expressions are obtained for Δ_m and Δ_c:

$$\Delta_m = \frac{R^2 \exp(-R)}{6\pi(1+S)}\left[\frac{3(R^2-R_0^2)}{R_0^2}\right] - F^2(1+S) \tag{34}$$

$$\Delta_c = \frac{-F^2 R_0^2 \exp(-R_0)}{6\pi} \tag{35}$$

while at the nuclei (say at B),

$$\Delta_n = \frac{-F_A^2 R_0^2 \exp(-2R_0)}{3\pi} \tag{36}$$

These equations show that for a π-π bond the δ function is *negative* in the internuclear region, and positive in a cylindrical region around this. The correlation between δ_c and the binding energy is therefore apparently restricted to σ bonds.

(v) The lone pair orbital

The δ function for a lone pair orbital on one atom is obtained by putting $A \equiv B$ and $S = 1$ in eqn. (25). For a lone pair in a $2p_z$ orbital this yields

$$\delta_{l.p.} = \frac{2R^2 \exp(-2R)}{\pi}\left[\cos^2\theta - \frac{F^2}{3}\right] \tag{37}$$

where $F^2 = 1$ if the orbital is unperturbed by the formation of a molecule. In such a case the surface $\delta_{l.p.} = 0$ is shaped like an infinite cone. If the lone pair orbital is affected by the rest of the molecule, then F is given by eqn. (14) as usual, and $\delta_{l.p.} = 0$ becomes a closed surface if $\gamma < 1$.

III. MULTIPLE BONDS

For the molecular electron density function a separation into σ and π parts is meaningful because those parts of the wave function belonging to the different symmetries do not interact. For the atomic density functions, especially when averaged over the angular co-ordinates, such a separation is not logical. It is however possible to define conventions whereby this division can be carried out, so that the δ function splits into parts that may be associated with σ or π bonds and lone pairs. All the s-orbital densities obviously contribute only to the σ portion of δ. It is therefore the way in which the density due to the p shells are split that has to be defined. As an example, consider the oxygen atom which has four electrons in the $(2p)$ shell. Averaged over all angular co-ordinates, their contribution to δ is proportional to $\frac{4}{3}r^2$ where r is the distance from the O atom. Two conventions for splitting up this term are proposed here.

In the first for example for the O_2 molecule, it is clear that of the four $2p$ electrons on each atom two eventually fill the lone pair orbital, one goes into the π bond and one into the σ bond. It is then natural to split up the terms proportional to $\frac{4}{3}r^2$ in the ratio of these contributions, namely $\frac{2}{3}r^2$ towards $\delta_{l.p.}$, $\frac{1}{3}r^2$ each towards δ_σ and δ_π. The partial δ functions then take the form discussed previously for two-electron bonds and the total δ is the sum of its parts:

$$\delta = \delta_{l.p.} + \delta_\sigma + \delta_\pi \tag{38}$$

Fig. 2 shows δ and δ_σ defined in this way for the O_2 molecule, using the SCF LCAO MO wave function of Kotani and collaborators.[17]* It is seen that δ_σ has

* The δ function for this wave function has also been published by Roux,[5] but there are some unexplained differences between the two pictures.

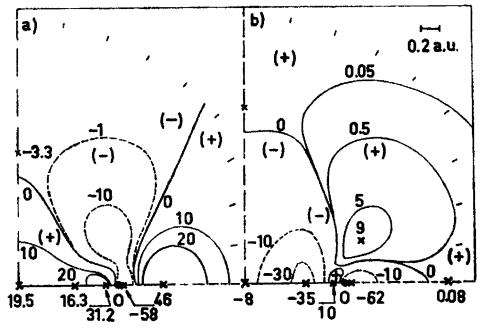


Fig. 2. O_2 molecule. δ and δ_σ ($10^2 \times$ values in a.u.) in a quarter plane. Calculated using the SCF function of Kotani *et al.*[17] a). The δ_σ function ((2*p*) shell contribution proportional to $\frac{1}{3}r^2$). b) The δ function.

the normal positive region between the nuclei, with a maximum at the centre. The large positive regions beyond the atoms suggest that the bond is mainly a $2p\sigma$-$2p\sigma$ bond. The only unexpected features are the larger maxima at 0.15 a.u. from each oxygen atom. The wave functions are not very accurate so close to the nuclei, and it is probable that these maxima are a result only of this inaccuracy. (The density is very large near the nuclei, and errors in δ are consequently also very large.) The total δ function is negative between the atoms in this case, but has been found positive in other multiple bonds. It would seem to depend solely on the relative importance of the σ and π bonds. For other multiple bonds see the δ functions for N_2 (Ref.[5]), NO, CO (Ref.[6]), C_2H_4, C_2H_2 (Ref.[7]), and CN, C_2 and C_4 (Ref.[12]).

The second convention is particularly useful for molecules, such as H_3O^+, which are planar or nearly planar and entirely σ bonded except for some lone pair orbitals perpendicular to the plane of the molecule. In such a case, I have argued that the two electrons in the $2p_z$ orbital (perpendicular to the plane of the molecule) remain polarised in the atomic case also. This leaves two electrons whose density is averaged in the xy plane. Thus the (2*p*) shell contributes terms proportional to $2z^2$ and $(x^2 + y^2)$ to $\delta_{l.p.}$ and δ_σ, respectively. It follows that $\delta_{l.p.} = 0$ and also that the additive property expressed in eqn. (38) is lost, since $2z^2 + x^2 + y^2$ is not equal to $\frac{4}{3}r^2$. However, the pictures of σ_σ obtained in this way are clearer and (provided it is stated which convention is used) it is only the clarity and simplicity of the pictorial representation

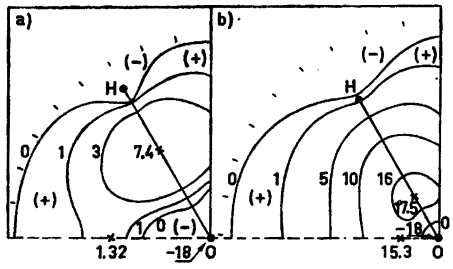


Fig. 3. Planar H_3O^+ ion. δ_σ ($10^2 \times$ values in a.u.) in the plane of the molecule. A quarter plane is shown. Calculated using Grahn's SCF function.[19] The charge distribution in the atomic case was assumed to be $O + 3H^{+1/3}$. a) The δ_σ function with the (2*p*) shell contribution proportional to $(x^2 + y^2)$ (or r^2 in the plane of the molecule). b) The δ_σ function with the 2*p*) shell contribution proportional to $\frac{2}{3}r^2$.

which should determine the way in which δ is split up. Figs. 3a and 3b show δ_σ in the plane of the molecule for H_3O^+. Compare these with Fig. 5, which shows δ for H_4O^{++}, when there are no lone pairs and $\delta \equiv \delta_\sigma$. Notice that the one bond in Fig. 5 and 3a look the same, whereas 3b looks rather different. Fig. 4 shows δ and the two δ_σ along the internuclear axis for OH^-. Compare this with the other heteronuclear diatomic molecule, LiH (Fig. 1).

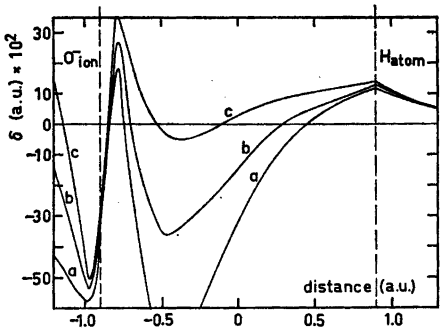


Fig. 4. OH^- ion. δ and δ_σ along the internuclear axis. Calculated using Rosenfeld's SCF function.[18] The charge distribution in the atomic case was assumed to be $O^- + H$. a) The δ function. b) The δ_σ function ($2p$) shell contribution proportional to z^2 (or y^2 along the axis). c) The δ_σ function ($2p$) shell contribution proportional to $\frac{1}{3}r^2$.

IV. RESULTS FOR OH BONDS

Figs. 5—12 show the results obtained for δ for strictly comparable wave functions in various planes through the molecules H_2O, H_3O^+, H_4O^{++} (all ten-electron systems).* Where possible, only half the plane is shown; the other half is to be obtained by reflection through the axis of symmetry shown dotted at the foot of the figures. The figures show a few contours of constant δ value (δ in atomic units), and the more important maxima, minima and saddlepoints. In all cases the OH distance is 1.8103 a.u., and it has been assumed that the oxygen atom is neutral in the noninteracting system of atoms. In all cases the same basic set has been used for molecular and atomic wave functions (*i.e.* $\gamma = F = 1$ in previous discussions; eqn. (8)).

The most obvious features of these figures are that all regions of positive δ are confined to a sphere of radius about 2.6 a.u. centred on the oxygen atom, and that all the atoms are in regions of negative δ. Furthermore $|\delta|$ is always quite small, except near the atoms (where large errors are likely, because of the inaccuracies of the wave functions.)

It should be mentioned that the actual electron density in the molecule (as opposed to δ) shows an almost uniform decrease from the origin outwards with only small "humps" at the positions of the hydrogen atoms. Thus ϱ itself offers no real clue as to the nature of the chemical bonds. In the case of δ, however, it is startlingly obvious that the regions of positive δ can be correlated with bonds or lone pairs. A detailed discussion now follows.

* The scale is shown in Fig. 5 and is the same for all the following figures. The semicircle is marked at ten degree intervals in each figure.

H_4O^{++}. It is easier to start the discussion with this molecule, since it contains no lone pairs, but only 'pure' OH bonds. The wave function is the SCF LCAO-MO (minimal basis set of Slater-type orbitals) described in Ref.[18] Fig. 5 shows δ in a plane containing two OH bonds. There is clearly an in-

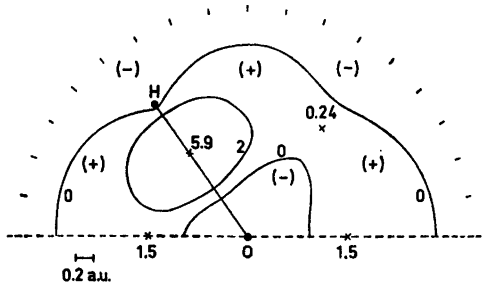
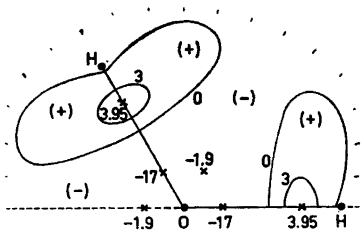


Fig. 5. Tetrahedral H_4O^{++}ion. δ ($10^2 \times$ values in a.u.) in a plane through two OH bonds. A half plane is shown. Calculated using Rosenfeld's SCF function.[18] The atomic charge distribution was assumed to be $O + 4H^{+1/3}$.

creased concentration of electrons (positive δ) in the region between O and each H, though these regions run into each other. The maximum value of δ is on the OH line ($\delta = 0.059$) and the saddlepoint is midway between the two OH bonds, ($\delta = 0.015$). The smallest values of positive δ are in the region beyond the oxygen atom in the HO line ($\delta = 0.0024$). The isobars of δ in the OH bond are such that the curve $\delta = 0.02$ is roughly ellipsoidal, with the major axis perpendicular to the OH bond. The position of δ_{max}, 1.15 a.u. from the oxygen atom (*i.e.* about two thirds along the OH bond), suggest that $H^{\frac{1}{3}+}$ is electronegative with respect to O (see the general discussion about eqn.(11) above).

H_3O^+. The wave functions in this case are SCF LCAO-MO (minimal basis set of Slater-type orbitals) taken from Grahn's paper,[19] for the planar molecule and that with an HOH angle of 110°. For the planar molecule (Fig. 6) it is obvious that the regions of positive δ are connected with the OH bond and with the lone pair $2p_z$ orbital above and below the plane of the molecule. As was discussed earlier, the latter can be removed in two ways, leaving in the



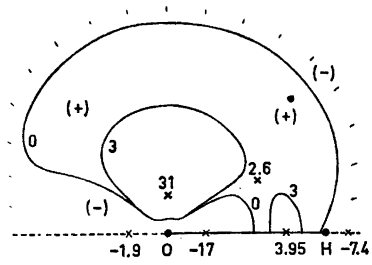


Fig. 6. Planar H_3O^+ion. δ ($10^2 \times$ values in a.u.) calculated using Grahn's SCF function.[19] The atomic charge distribution was assumed to be $O + 3H^{+1/3}$. a) in the plane of the molecule. b) in a plane perpendicular to that of the molecule, and passing through one OH bond.

plane of the molecule the function δ_σ as shown in Fig. 3. As for the cone shaped region of positive δ in Fig. 6b, corresponding to the lone pair, it is interesting to see how closely eqn. (37) comes to predicting its contours. According to eqn. (37) the cone formed by the surface $\delta = 0$ has a half angle of 54°44′, compared to about 55° in Fig. 6. Furthermore the maximum value of δ in this region occurs at 0.43 a.u. from the oxygen atom, which is where the $(2p)$ shell reaches its maximum. The fact that the surface $\delta = 0$ is closed in Fig. 6 shows that the lone pair is slightly affected by the rest of the molecule. It also indicates that the approximation discussed previously as case II ($\gamma \neq 1$) is equivalent to using an extended basis set to describe the molecular wave function. As has been mentioned before there is a close similarity between Fig. 4a and Fig. 5, showing the "pure" OH bonds in H_3O^+ and H_4O^{++}, respectively. The only significant difference is that the marked contour enveloping almost the same volume now has a value 0.03 instead of 0.02. The maximum is 0.073 instead of 0.059.

Figs. 7 and 8 show the δ function for H_3O^+ for the HOH angle equal to 110°. The most interesting feature is in Fig. 8, where it is clearly seen that the

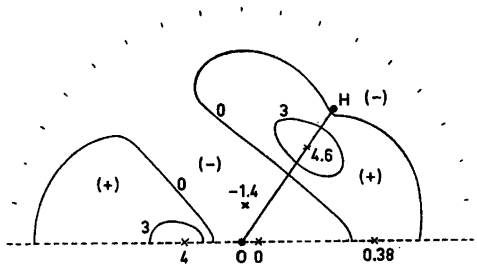


Fig. 7. H_3O^+ion, $\angle$HOH = 110°. δ ($10^2 \times$ values in a.u.) in a HOH plane. Calculated using Grahn's SCF function.[19]

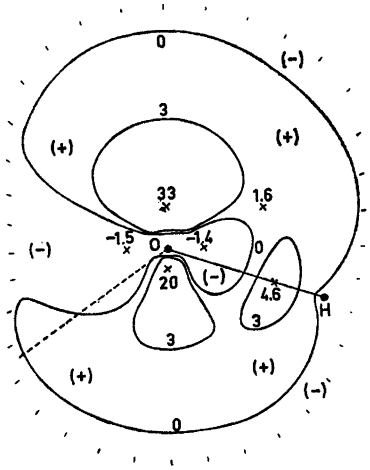


Fig. 8. H_3O^+ion, $\angle$HOH = 110°. δ ($10^2 \times$ values in a.u.) in a plane perpendicular to the HHH plane, passing through one OH bond. The dotted line is the projection onto this plane of the other two OH bonds.

OH "bonds squeeze" the lone pair from between them, with a consequent increase in the lone pair region above the oxygen atom (maximum 0.33 instead of 0.31 for planar H_3O^+; between the OH bonds the maximum in the lone pair region is only 0.20). Also, the half of the lone pair orbital lying between the OH bonds has its maximum closer to the O atom than the other half. The 0.33 maximum is at 0.43 a.u. from O, *i.e.* at the maximum for the $(2p)$ shell. Since in this case the $2p_z$ orbital does interact with the other orbitals in the wave function, it is not possible accurately to remove the effect of the lone

pair, as was done for the planar molecule in order to obtain the "pure" OH bond. The coefficient of the $2p_x$ orbital in the lone pair MO is 0.9397. If, therefore, instead of placing 2 electrons in the $2p_x$ orbital in the noninteracting system of atoms, one puts in only $2 \times (0.9397)^2$, then the $2p_x$ contribution to the electron density in the molecular and the noninteracting systems will approximately cancel. In general terms, if $2n$ electrons are assumed to be in the $2p_x$ orbital in the atomic wave function, then it is easily found for a system with four $(2p)$ electrons that

$$\delta_\sigma = \delta + (3n-2)(1-\cos^2\theta)\frac{r^2\alpha^5}{3\pi}\exp(-2\alpha r) \tag{39}$$

where θ is the angle measured from the z axis and α is the exponent of the $(2p)$ shell. This formula applied to H_3O^+ (110°) (with $n = (0.94)^2 = 0.884$ and $\theta = 72°$) gives a maximum of 0.062 for δ_σ in the OH bond compared with 0.046 for δ. For $n = 1$ eqn. (39) would give 0.071 for the same quantity. In both planar and non-planar H_3O^+ the maximum value of δ_σ in the OH bond again occurs at about 1.15 a.u. from the oxygen atom, despite the fact that the charge in the hydrogen atom is only $\frac{1}{3}$ instead of $\frac{1}{2}$ as in H_4O^{++}. It would therefore seem that the position of the maximum along the axis is not very sensitive to the differences in electronegativity between the oxygen atom and either $H^{+\frac{1}{2}}$ or $H^{+\frac{1}{3}}$. The maximum value of δ occurs at 1.3 and 1.35 a.u. from the oxygen atom in H_3O^+ (110°), and H_3O^+ (planar), respectively.

H_2O. The wave functions are the SCF LCAO-MO (minimal basis set Slater-type orbitals) for $\angle HOH = 105°$ and 120° as published by Ellison and Shull.[20] For the molecule with the HOH angle 105° (Figs. 9, 10, 11a), positive regions

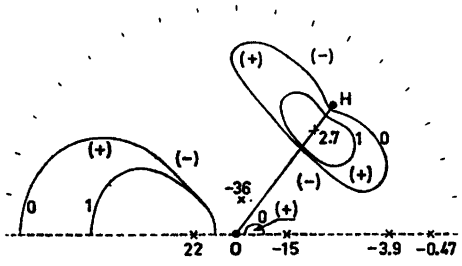


Fig. 9. H_2O molecule, $\angle HOH = 105°$. δ ($10^2 \times$ values in a.u) in the plane of the molecule. Calculated using Ellison and Shull's SCF function.[20]

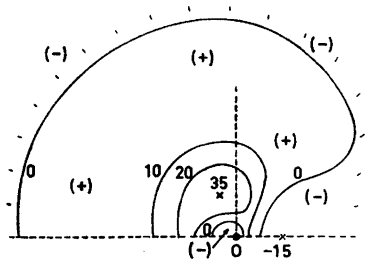


Fig. 10. H_2O molecule, $\angle HOH = 105°$. δ ($10^2 \times$ values in a.u.) in a plane perpendicular to that of the molecule and bisecting the angle HOH.

of δ are again clearly associated with the lone pairs and the OH bonds. There are, however, a few interesting deviations from the picture described so far. Firstly, the OH bond is much "thinner", as if there were a repulsion between it and the lone pair region. Secondly, the lone pair maxima occur above and below the plane of the molecule, at an angle of about 15° from the z axis, away from the z axis, away from the hydrogen atoms (the z axis is the one

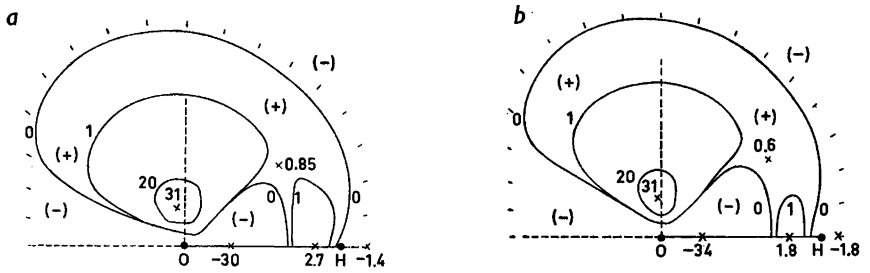


Fig. 11. a) H_2O molecule, $\angle HOH = 105°$. δ ($10^2 \times$ values in a.u.) in a plane perpendicular to that of the molecule, and passing through an OH bond. b) H_2O molecule, $\angle HOH = 120°$. δ ($10^2 \times$ values in a.u.) in the same plane as for a). Calculated from Ellison and Shull's SCF function.[20]

perpendicular to the plane of the molecule. It is in fact the x axis as defined by Ellison and Shull). Fig.10 shows this well. Another indication that the lone pair is considerably perturbed by the OH bonds is that the maximum occurs at a greater distance from the oxygen atom (0.52 a.u. instead of 0.43 a.u.) than the maximum of the ($2p$) shell. The value of the maximum itself (0.35 a.u.) is larger than in the "pure" lone pair of planar H_3O^+ (0.31). However, in the wave function the $2p_z$ orbital does not interact with the others, and it should therefore be possible to subtract its contribution to δ in the plane of the molecule as before. When this is done, the maximum value of δ_σ in the OH bond is still on the internuclear axis and has a value of 0.049 compared to $\delta = 0.027$. The distance of the maximum from the oxygen atom is 1.2 a.u., somewhat larger than in the other molecules, which is unexpected since O should be more electronegative with respect to H than with respect to $H^{+\frac{1}{2}}$ or $H^{+\frac{1}{3}}$. This is further evidence that the OH bond and the second lone pair region (which cannot be allowed for in any realistic way since it involves the same atomic orbitals as form the OH bonds) repel each other strongly. (Compare also with the discussion on the gross charge of the oxygen atom in Ref.[18]).

When one turns to H_2O with $\angle HOH = 120°$ (Figs. 11b, 12) the most important finding is that despite the change in the HOH angle of 15°, the picture of the δ function in the plane of the molecule remains essentially unchanged. (It must be remembered that Ellison and Shull's coefficients are rounded off to the fourth decimal place, and since δ itself is a small difference between

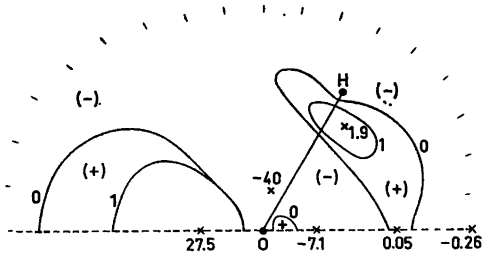


Fig. 12. H_2O molecule, $\angle HOH = 120°$. δ ($10^2 \times$ values in a.u.) in the plane of the molecule.

larger numbers involving these coefficients, small changes in δ, say of the other of 10^{-3}, are not very significant). The maximum in the OH bond is exactly at the same place as in the previous case, instead of having followed round with the internuclear axis (*cf.* Figs. 9 and 12). It is one of the unsolved problems of the SCF method that the energy minimum in this approximation is found for an HOH angle of 120° rather than for the experimental value of 105°. Other methods used to obtain wave functions do predict the correct configuration, and Bader and Jones [21] have published electron density maps for H_2O (105°) obtained by minimising the net forces acting on the nuclei. For their best wave function they obtain a density distribution suggestive of bent bonds. This result is not supported by the pictures of the δ function obtained here, since the angle between the maxima is 105° in both cases ($\angle HOH = 105°$ and 120°).

OH^-. Fig. 4 shows the δ function and the δ_σ functions defined in the two ways mentioned above, along the internuclear axis. Again an SCF LCAO-MO function (minimal basis set of Slater-type orbitals) was used.[18] In this case the OH bond is no longer similar to that of H_4O^{++} and the maxima occur at the H nucleus, just in front of the oxygen atom and behind the oxygen atom. The first and last maxima correspond to an OH bond with considerable $2p\sigma$ character. The second maximum is probably an artifact resulting from the use of an approximate wave function. The δ function also shows that H is electronegative with respect to O^-, which is not surprising. A comparison with the results for LiH shows that the position of the maximum at the H nucleus may be a result of using the same exponents in the molecular and atomic functions (compare curves *a* and *c* of the LiH results). It seems that for diatomic molecules with large dipole moments the δ functions shown in Figs. 1 and 3 are typical.

V. DISCUSSION

(i) Maximum δ and bond strength

Table 3 shows the bond strength of an OH bond (dissociation energy divided by the number of bonds) for the different molecules, compared with the overlap population per bond [2] and with the maximum value of δ (or δ_σ in those cases where this better represents the OH bond). It is seen that there

Table 3. Relation between δ_σ (max) and the bond strength.

molecule	bond strength (a.u.)	δ_σ (max) (a.u.)	Overlap population per bond
H_2O (105°)	0.114	0.049	0.415
H_3O^+ (planar)	0.216	0.074	0.514
H_3O^+ (110°)	0.202	0.062(0.071)	0.483
H_4O^{++}	0.146	0.059	0.409

is a correlation between the bond strength and both the overlap and the δ_σ function, but that the latter is much better. (Note that δ_σ is defined by the second convention discussed in the third section). The OH^- molecule is not included because the δ function in the OH bond is so different.

The correlation between δ_{max} and the bond strength found here confirms the similar results of the calculations made on the simple symmetrical bonds in section II.

(ii) Total increase in electric charge in bonds

A very rough estimate of the total increase of charge in the positive δ region can be obtained by assuming the region to be an ellipsoid with a constant mean value of δ. For the OH bond in H_3O^+ (planar) this estimate gives $\int_+ \delta \, d\tau \approx 0.1$ electrons per OH bond. In the lone pair a similar estimate yields $\sim$0.6 electrons (for a pure lone pair the answer should be $\frac{2}{3}$, since there are assumed to be 2 electrons in that orbital in the molecule, but only $\frac{4}{3}$ on average in the noninteracting oxygen atom). The change in electron concentration on bond formation is therefore quite small.

(iii) Distortion of atomic orbitals

In the planar H_3O^+ molecule, δ_σ (defined by the second method of section III) is negative above and below the oxygen atom. This shift of the electrons into the plane of the molecule could be described in terms of a distortion of the (1*s*) and (2*s*) orbitals into ellipsoids. Similarly the hydrogen (1*s*) orbital can be described as being distorted and pulled in towards the oxygen atom, thus contributing to the increase in electron concentration between the atoms.

(iv) Conclusion

The contours of the δ functions for these molecular orbital wave functions show up in a most remarkable way the localised position of the bonds. This is a most satisfying result, since, as was suggested in the introduction, the concept of a bond has been in danger of being swamped and hidden by the increased complexity of the accurate wave functions obtained in recent years. The present analysis shows that the connection is very close though hidden. In my opinion the abstraction of chemical ideas from such wave functions will best be done along the lines indicated in this paper.

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