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Population Analysis Based on Occupation Numbers of Modified Atomic Orbitals (MAOs)

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A new interpretational scheme is proposed for the analysis of molecular wavefunctions. Starting from the molecular density operator we first construct a minimal set of MAOs from the requirement that the MOs can be represented as closely as possible by the MAOs. We then use the MAOs to compute atomic occupation numbers N and shared electron numbers σ. The molecular density is then discussed in terms of N and σ. This approach has the following advantages: 1) it is generally applicable, 2) the quantities N and σ are virtually basis set independent, 3) the quantities N and σ fulfil the intuitively expected boundary conditions, 4) the simultaneous consideration of N and σ allows for a more reliable description of chemical bonding than consideration of atomic charges only.

Key words: Population analysis – Occupation numbers – Modified AOs

1. Introduction

The characterization of an electronic molecular wavefunction by a small set of quantities referring to atoms and bonds – like atomic gross charges and overlap populations obtained from a population analysis [1–6] – provides the simplest analysis of a molecule in a given electronic state. A population analysis cannot be derived from the principles of Quantum Mechanics, however, since "atomic charges" – to give an example – are not measurable quantities of a molecule. Some arbitrariness is consequently inevitable if we want to discuss a molecule in terms of atoms and bonds.

In order that an interpretational scheme is physically and mathematically adequate, it appears reasonable to require that the following conditions are met

1) internal consistency and general applicability
2) certain boundary conditions should be met (e.g. the gross charge of an AO should be positive and smaller or equal to two)
3) features of chemical bonding should be reflected.

Condition 1) requires especially that the results of an analysis should not depend on the actual representation of the corresponding wavefunction, i.e. it should be basis set independent.

The description of chemical bonding (condition 3) by quantities like the amount of electron sharing or the overlap population should not only reflect features of bonding but also indicate to which degree the atoms have lost their identity in forming a molecule.

This furthermore provides a measure for the uncertainties inherent in a definition of atomic charges.

We note that the Mulliken Population Analysis (MPA) does certainly not meet requirements 1) and 2), as will be discussed shortly in Sect. 2 of this work.

In the present work we confine ourselves to the discussion of one-particle properties. This restriction appears to be reasonable since bonding is essentially a one-particle effect [7]. Condition 1) then requires that an analysis should be based on the one-particle density operator **D**.

The population analysis described in this work is based on the following idea: In order to calculate accurate densities it is necessary to use extended basis sets which furthermore - for technical reasons - have no direct physical meaning in general. One therefore should not insist to analyze **D** in terms of this extended basis set but to use for this purpose a (different) AO basis set φ_ν of some physical significance [8] (the problems to define such a set φ_ν of AOs is discussed in more detail in Sect. 3).

A necessary condition for such a procedure to be meaningful is that the φ_ν represent the original density operator **D** sufficiently well, which is equivalent to the condition that $\mathrm{tr}\mathbf{DP} \approx$ number of electrons, where **P** denotes the projector onto the space spanned by the AOs φ_ν. Besides defining a minimal AO basis with properties just mentioned, the difficulties of a population analysis are then essentially due to the nonvanishing interatomic overlap of the AOs φ_ν which in turn is intimately connected with chemical bonding.

The only quantities with a direct physical meaning that can be constructed from **D** and the φ_ν are the occupation numbers $N_{\nu\nu}$, which are the diagonal elements of the matrix **N**

$$N_{\nu\mu} = \langle \varphi_\nu | \mathbf{D} | \varphi_\mu \rangle \tag{1}$$

D may also be specified by the matrices **Q**(1) and **Q**(2) defined as follows (we tacitly assume here that **D** may be represented by the φ_ν, this point will be discussed in more detail in Sect. 3)

$$\mathbf{D} | \varphi_\nu \rangle = \sum_\lambda \mathbf{Q}(1)_{\lambda\nu} | \varphi_\lambda \rangle \tag{2}$$

$$\mathbf{D} = \sum_{\nu,\mu} | \varphi_\nu \rangle \mathbf{Q}(2)_{\nu\mu} \langle \varphi_\mu | \tag{3}$$

The matrices **Q**(1) and **Q**(2) are related through

$$\mathbf{N} = \mathbf{SQ}(1) = \mathbf{SQ}(2)\mathbf{S} \tag{4}$$

where **S** denotes the overlap matrix of the φ_ν.

We note that the diagonal elements $\mathbf{Q}(1)_{\nu\nu}$ and $\mathbf{Q}(2)_{\nu\nu}$ are usually referred to as gross charges and net charges of AOφ_ν [1, 2]. As the $\mathbf{Q}(1)_{\nu\nu}$ and $\mathbf{Q}(2)_{\nu\nu}$ have no direct physical meaning it appears reasonable to base an interpretational scheme on the occupation numbers only. The $N_{\nu\nu}$ furthermore have the advantage to depend on **D** and φ_ν only, whereas the $\mathbf{Q}(1)_{\nu\nu}$ depend - via the overlap-matrix - on all other AOs φ_ν, see Eq. (4). A rather small change in φ_μ may lead to rather drastic changes in $S_{\nu\mu}$ and, hence, in $\mathbf{Q}(1)_{\nu\nu}$ which is the reason for the strong basis set dependence of the results of MPA.

The use of occupation numbers for the purpose of interpretation of molecular electron distributions has first been proposed by Davidson [8] and recently been worked out and discussed by Roby [9].

In order to give the reader a rough idea of the procedures used in a population analysis based on occupation numbers let us discuss briefly the H_2-molecule [8]. In the MO description we have a doubly occupied MO ψ which is approximately given as the sum of the 1s-AOs φ_A, φ_B of the hydrogen atoms.

$$\psi = (\varphi_A + \varphi_B)/\sqrt{(2 + 2S)} \tag{5}$$

The density operator **D** is then

$$\mathbf{D} = 2 \,|\, \psi \rangle \langle \psi \,| \tag{6}$$

which gives the occupation $N(H)$ (note that $S \approx 0.7$)

$$N(H) = \langle \varphi_A \,|\, \mathbf{D} \,|\, \varphi_A \rangle = 1 + S \approx 1.7 \tag{7}$$

For a Heitler-London wavefunction one obtains [8]

$$N(H) = \frac{1 + 3S^2}{1 + S^2} \approx 1.66 \tag{8}$$

The Eqs. (7) and (8) show in a quantitative way that in forming H_2 the hydrogen atoms have completed to a considerable extent the helium shell by electron sharing.

The sum of occupation numbers exceeds the number of electrons, $N = 2$, and the excess $\sigma(H, H')$

$$\sigma(H, H') = N(H) + N(H') - N \approx 1.4 \tag{9}$$

is a measure of the amount of electron sharing and the bond strength [8].

From the quantities $N(H)$ and $\sigma(H, H')$ we can then compute an atomic charge $R(H)$ in dividing σ equally between the atoms, which is, of course, a trivial procedure for a homonuclear molecule

$$R(H) = N(H) - \tfrac{1}{2}\sigma(H, H') = 1$$

This very simple example demonstrates already how the use of occupation numbers allows for a discussion of terms like "completion of noble gas shells" by "electron sharing", which play an important role in the thinking of chemists.

2. Population Analysis Based on Occupation Numbers

In this section we first repeat briefly some basic definitions (e.g. of the occupation $N(A)$ of atom A) which were already given by Davidson [8] and by Roby [9], and then discuss some properties of the corresponding quantities.

The considerations of this section are rather formal since we essentially show that the various quantities fulfil the expected boundary conditions and inequalities as required in condition 2) introduced in the introduction.

Let φ_ν denote the set of AOs which is to be used in the interpretation of the molecular density. Without loss of generality we may assume that AOs corresponding to the same atom are orthonormal:

$$\langle \varphi_\nu \,|\, \varphi_\mu \rangle = \delta_{\nu\mu} \tag{10}$$

if φ_ν, φ_μ are centered on the same atom.

The projection operator $\mathbf{P}_A$ onto the space spanned by the φ_ν of atom A is then given as

$$\mathbf{P}_A = \sum_{\nu \in A} |\varphi_\nu\rangle \langle \varphi_\nu| \tag{11}$$

Let $\mathbf{S}_{AB}$ denote the overlap matrix of the set of AOs of atom A and B

$$(\mathbf{S}_{AB})_{\nu\mu} = \langle \varphi_\nu | \varphi_\mu \rangle \qquad \nu, \mu \in A, B \tag{12}$$

The projection operator $\mathbf{P}_{AB}$ onto the space spanned by the AOs of A *and* B is then

$$\mathbf{P}_{AB} = \sum_{\nu,\mu} | \varphi_\nu \rangle (\mathbf{S}_{AB}^{-1})_{\nu\mu} \langle \varphi_\mu | \tag{13}$$

We similarly construct the projection operators $\mathbf{P}_{ABC}, \mathbf{P}_{ABCD}, \ldots$, associated with a triple of atoms A, B, C, and so on. The projection operator onto the space spanned by all AOs will be denoted by $\mathbf{P}$

$$\mathbf{P} = \sum_{\nu,\mu} | \varphi_\nu \rangle (\mathbf{S}^{-1})_{\nu\mu} \langle \varphi_\mu | \tag{14}$$

$$\mathbf{S}_{\nu\mu} = \langle \varphi_\nu | \varphi_\mu \rangle \tag{15}$$

The analysis of $\mathbf{D}$ in terms of φ_ν will only be meaningful if $\mathbf{D}$ is represented by the φ_ν in the sense of Eq. (2) or (3), which is equivalent to the requirement

$$\mathrm{tr}\mathbf{DP} = N \tag{16}$$

where N = number of electrons.

We now define [8, 9] the occupation $N(A)$ of atom A:

$$N(A) = \mathrm{tr}\mathbf{DP}_A \tag{17}$$

and further the "atom pair occupation" $N(AB)$, etc.

$$N(AB) = \mathrm{tr}\mathbf{DP}_{AB} \tag{18}$$

$$N(ABC) = \mathrm{tr}\mathbf{DP}_{ABC} \tag{19}$$

From the occupation numbers one can further compute "shared electron numbers" [9] corresponding to a pair of atoms, $\sigma(AB)$, a triple of atoms, $\sigma(ABC)$, which are conveniently defined in the following way:

$$\sigma(AB) = N(A) + N(B) - N(AB) = \sum_X N(X) - \tfrac{1}{2} \sum_{X,Y}{}' N(XY) \tag{20}$$

$$\sigma(ABC) = \sum_X N(X) - \frac{1}{2!} \sum_{X,Y}{}' N(XY) + \frac{1}{3!} \sum_{X,Y,Z}{}' N(XYZ) \tag{21}$$

and so forth until finally all atoms are involved

$$\sigma(AB \ldots F) = \sum N(X) - \tfrac{1}{2} \sum{}' N(XY) + \ldots \pm N(AB \ldots F) \tag{22}$$

The sums in Eq. (20–22) are understood to run only over the atoms specified in the argument of σ on the left hand side, the primes indicate that terms X = Y etc. are omitted.
By virtue of Eq. (16) we can rewrite (22) in the form

$$N = \sum_A N(A) - \frac{1}{2!} \sum_{AB}{}' \sigma(AB) + \frac{1}{3!} \sum_{ABC}{}' \sigma(ABC) \ldots \tag{23}$$

as is easily verified.

We note that the $\sigma(ABC)$ and σ's depending on even more atoms are in general negligibly small except for molecules with three center bonds as H_3^+ and B_2H_6.

The formal definition of shared electron numbers $\sigma(AB), \sigma(ABC), \ldots$, is, of course, based

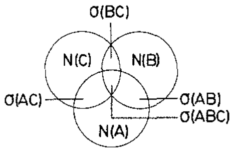

Fig. 1. Schematic representation of atomic occupations $N(A)$ and shared electron numbers $\sigma(AB)$, $\sigma(ABC)$

on simple set theoretical considerations as visualized in Fig. 1 for a triatomic molecule. Such a graphical representation breaks down, however, if some of the σ's are negative.

The corresponding shared electron numbers are intuitively expected to be related to effects of two center, three center bonds [9].

We want to point out that the quantities $N(A)$, $N(AB)$, $\sigma(AB)$ etc. have a definite meaning for any given set of AOs φ_ν in the sense that they refer to the molecular density **D** only and do not depend on the actual representation of **D** by one or the other basis.

A decomposition of $N(AB)$ or $\sigma(AB)$ into additive contributions referring to AOs or groups of AOs at the respective atoms is not possible in general as is obvious from the definitions (12), (13), (17-20). No problems are encountered if the AOs φ_ν may be divided into mutually orthogonal sets like σAOs and πAOs in planar molecules. In this case one can immediately write down the σ and π contributions to $\mathbf{P}_A$ and $\mathbf{P}_{AB}$ and then compute the corresponding occupations $N_\sigma(A)$, $N_\pi(A)$, etc. and finally the shared electron numbers

$$\sigma_\sigma(AB) = N_\sigma(A) + N_\sigma(B) - N_\sigma(AB) \tag{24}$$

$$\sigma_\pi(AB) = N_\pi(A) + N_\pi(B) - N_\pi(AB) \tag{25}$$

which add up to the total $\sigma(AB)$

$$\sigma(AB) = \sigma_\sigma(AB) + \sigma_\pi(AB)$$

We may consider Eq. (23) as a partitioning of the total number of electrons which could be used to define atomic charges. This requires the distribution of $\sigma(AB)$, $\sigma(ABC)$, etc. on the corresponding atoms. In the case of covalent or at least dominantly covalent bonds it is reasonable - though arbitrary - to divide the σ's equally between the atoms involved. This procedure would lead to the following definition of an electronic charge $R(A)$

$$R(A) = N(A) - \tfrac{1}{2} \sum_{B}{}' \sigma(AB) + \frac{1}{3!} \sum_{BC}{}' \sigma(ABC) - \dots \tag{26}$$

$$\sum_{A} R(A) = N \tag{27}$$

If three-center terms are negligible, Eq. (26) reduces to

$$R(A) = N(A) - \tfrac{1}{2} \sum_{B}{}' \sigma(AB) \tag{28}$$

The definition (26) of $R(A)$ depends on the division of shared electrons equally between participating atoms, which is an arbitrary procedure. Since the present approach does not require a definition of an atomic charge as $R(A)$, we will consider $R(A)$ only occasionally.

2.1. *Properties of* $N(A)$, $N(AB)$, $\sigma(AB)$

We now show that the quantities defined in the preceding section are formally reasonable in the sense that certain physically expected inequalities are in fact fulfilled.

Let n_A denote the number of AOs at atom A. We can write down immediately the following obvious inequalities

$$0 \leqslant N(A) \leqslant 2n_A \tag{29}$$

$$0 \leqslant N(AB) \leqslant 2(n_A + n_B) \tag{30}$$

$$0 \leqslant N(A_1 \ldots A_m) \leqslant 2 \sum_{\nu=1,m} n_{A_\nu} \tag{31}$$

and further

$$N(A) \leqslant N(AB) \leqslant N(ABC) \tag{32}$$

From Eq. (32) and the definition of $\sigma(AB)$, Eq. (20), we obtain

$$-N(AB) + \max[N(A), N(B)] \leqslant \sigma(A, B) \leqslant \min[N(A), N(B)] \tag{33}$$

from which one gets immediately the following bounds which are poorer, however,

$$-N(AB) + \tfrac{1}{2}[N(A) + N(B)] \leqslant \sigma(AB) \leqslant \tfrac{1}{2}[N(A) + N(B)] \tag{34}$$

$$|\sigma(AB)| \leqslant N(AB) \tag{35}$$

The absolute value of the shared electron number $|\sigma(AB)|$ cannot exceed the occupation $N(AB)$. The case

$$\sigma(AB) = \pm N(AB) \tag{36}$$

is in fact realized for the MO

$$\psi = (\varphi_A \pm \varphi_B)(2 \pm 2S)^{-1/2} \tag{37}$$

in the limit

$$S = \langle \varphi_A | \varphi_B \rangle \to 1 \tag{38}$$

The proof given by Roby [9] that $\sigma(AB) \geqslant 0$, is not correct, the logical error is in relationship (*B* 15) of Ref. [9]. The inequalities (38), (39) and (45) of [9] are also at least partially incorrect for similar reasons.

We mention that it can also be shown that the atomic charges $R(A)$ defined in Eq. (26) fulfil the following inequality which is analogous to (29)

$$0 \leqslant R(A) \leqslant 2n_A \tag{39}$$

The proof is tedious and will be omitted.

We point out that bounds like those for $N(A)$ and $\sigma(AB)$ cannot be derived in general for the corresponding quantities of a MPA. This is most drastically seen from the following quite extreme example. Consider a doubly occupied MO

$$\psi = \alpha\varphi_a + \beta\varphi_b \tag{40}$$

in the limit

$$S = \langle \varphi_a | \varphi_b \rangle = 1 \tag{41}$$

which leads to the normalization condition

$$\alpha + \beta = 1 \tag{42}$$

In this case one gets

$$N(\mathrm{A}) = N(\mathrm{B}) = N(\mathrm{AB}) = \sigma(\mathrm{AB}) = 2 \tag{43}$$

$$R(\mathrm{A}) = R(\mathrm{B}) = 1 \tag{44}$$

Eq. (43) expresses correctly the fact that the electrons are completely shared between φ_a and φ_b and (44) appears to be a reasonable result for an atomic charge. The MPA yields

$$Q(\mathrm{A}) = 2\alpha \qquad Q(\mathrm{B}) = 2\beta \tag{45}$$

$$p_{\mathrm{AB}} = 4\alpha\beta \tag{46}$$

As α and β may vary between $\pm\infty$ (Eq. (42) is the only constraint) $Q(\mathrm{A})$ and $Q(\mathrm{B})$ are totally unspecified and p_{AB} may have any value between $-\infty$ and $+1$.

This is clearly an unreasonable example - for which the MPA was not conceived - but it expresses in a drastic way the dependence of the MPA on the actual representation of the wavefunction.

3. Definition of MAOs

The applicability of the population analysis based on occupation numbers hinges critically on the problem to find an AO basis set (denoted φ in the preceding section) suited for this purpose. For an analysis of HF wave function it is near at hand to use HF-AOs, as has been proposed by Davidson [8]. Since the HF-AOs do not span the space of occupied MOs in general, one has (instead of the desired Eq. (16))

$$\mathrm{tr}\mathbf{DP} = N - \epsilon,\ \epsilon > 0 \tag{47}$$

where ϵ has been denoted "unassigned charge" [8]. For some diatomic molecules investigated [8], ϵ is typically of the order 0.2. This shows on one hand that the HF-AOs are quite useful, but on the other hand it would be desirable to have a smaller unassigned charge, say $\epsilon \lesssim 0.05$, which would remove uncertainties in the interpretation [8]. The use of HF-AOs has the further disadvantage that effects like orbital contraction (or extension) and polarization, which are of vital importance for a reliable description of chemical bonding, are not explicitly considered.

In order to reduce the unassigned charge and to account for the change of AOs on bond formation there are basically two possibilities

1) one uses a more extended basis set
2) one modifies the AOs to minimize ϵ.

Let us first consider the prospects of employing extended basis sets. In the extreme limit that the atomic basis φ_ν on atom A becomes complete one has $\mathbf{P}_{\mathrm{A}} = 1$, compare Eq. (11), and consequently $N_{\mathrm{A}} = N$ (total number of electrons in the molecule). The occupation numbers would not provide any information in this case.

From this point of view we would not support a proposal of Roby [9], to use the NOs with non-vanishing occupation of suitable atomic states as a basis for the interpretation of molecular wave functions, since there are indications that these NOs form a complete set [10].

Even the use of slightly extended basis sets causes problems as is apparent from the following example. Roby [9] has computed atomic occupations $N(\mathrm{A})$ and shared electron numbers $\sigma(\mathrm{AB})$ for a series of diatomic molecules. For Li_2 and Be_2 the latter author employs a set of three AOs for this purpose ($1s$, $2s$, $2p\sigma$). The result is then $\sigma(\text{Li, Li}) = 1.74$ and $\sigma(\text{Be, Be}) = 1.69$. This would mean - compare with $\sigma(\text{H, H}) = 1.4$, Eq. (9) - that rather saturated bonds should be formed in Li_2 and Be_2, which is certainly not the case for Be_2. Under such circumstances σ could not be considered a reliable measure of bond strength, in contradiction with the claims of Roby [9].

The present authors have concluded from this kind of considerations that the AO set used for the interpretation of molecular densities should be kept as small as possible. This then necessarily requires a modification of AOs in order to keep the unassigned charge ϵ sufficiently small.

We consequently propose the following procedure. For a given density operator **D** we construct modified AOs (MAOs) φ_ν from the requirement

$$\mathrm{tr}\mathbf{DP} = \max \tag{48}$$

which is equivalent to a minimization of ϵ, compare Eq. (47). The projection operator **P** is obtained from the φ_ν according to Eq. (14).

The MAOs determined from (48) for molecular HF densities will usually be quite close to the unmodified HF-AOs. Since the latter yield $\epsilon \lesssim 0.2$, one certainly needs only minor modifications to reduce ϵ to values close to zero.

We further conclude that it will be sufficient in general to use a minimal set of MAOs only. This is by no means necessary, however. We rather consider the unassigned charge ϵ as an indication which helps to decide which number of MAOs should be used. This procedure may be explained for PH_5 as an example of a pentavalent phosphorous compound. For a set of 9 MAOs on P - corresponding to $1s$, $2s$, $2p$, $3s$, $3p$ - and a single MAO on H we get $\epsilon = 0.21$. The rather large value of ϵ indicates the necessity to increase the number of MAOs on P to 10 (yielding $\epsilon = 0.03$), in agreement with the conception of a pentavalent central atom.

An extended set of MAOs may also be necessary for the interpretation of densities **D** obtained from correlated wavefunctions.

We note that MAOs have originally been introduced in a different context by Mulliken [11]. The determination of MAOs according to (48) could be called an *a posteriori* method, for a discussion of *a priori* methods we refer the reader to Ref. [12].

Let us now describe some more details of the construction of MAOs.

In order to maintain the atomic character of the MAOs φ_ν, we expand φ_ν in a set of atomic functions f_μ, in an obvious notation

$$\varphi_\nu = \sum_\mu f_\mu C_{\mu\nu}, \qquad \text{for } \nu, \mu \in \text{A} \tag{49}$$

For the analysis of an LCAO wavefunction it is convenient to expand the MAOs in the very same basis as used originally, though this is by no means necessary.

Eq. (49) may be written in a compact form as

$$\boldsymbol{\varphi} = f\mathbf{C} \tag{50}$$

where **C** is blocked such that

$$\mathbf{C}_{\nu\mu} \neq 0 \qquad \text{only if } \nu \in \text{A}, \mu \in \text{A}. \tag{51}$$

The explicit form for trDP now reads

$$\mathrm{tr}\mathbf{DP} = \mathrm{tr}\mathbf{NC}[\mathbf{C}^{+}\mathbf{FC}]^{-1}\mathbf{C}^{+} \tag{52}$$

where $\mathbf{N}$ is defined in (1) and $\mathbf{F}$ denotes the overlap matrix

$$\mathbf{F}_{\nu\mu} = \langle f_\nu | f_\mu \rangle \tag{53}$$

The requirement (48) together with the constraint (51) specifies only the space spanned by the MAOs located at the same atom and the latter may therefore be chosen orthonormal as indicated in (10). We then have still a unitary transformation at our disposal which may be chosen to maintain σ-π separation.

In the appendix we describe a generally applicable procedure to determine MAOs according to (48) and (49).

4. Applications

We will now apply the theory developed in the preceding Sects. 2 and 3. In Sect. 2 we have shown that a population analysis based on occupation numbers is formally reasonable, condition 2) of the introduction. Since the method is clearly generally applicable we now want to demonstrate that the PA based on occupation numbers of MAOs (as determined in the way described in Sect. 3) is internally consistent and also reflects the essential features of chemical bonding, conditions 1) and 3).

4.1. Atomic Populations for H_2O*, Computed with Different Basis Sets*

In this subsection we want to demonstrate that a population analysis based on occupation numbers of MAOs provides a consistent and sufficiently basis set independent characterization of molecular densities. For this purpose we have performed a series of HF computations for H_2O with a number of different basis sets, taken in part from Huzinaga's tables [13]. The very same basis was then used in the determination of MAOs according to Eqs. (48) and (49). The use of identical basis sets has some obvious practical advantages but is by no means necessary.

The results of these computations are listed in Table 1. In the first five rows we have excluded polarization functions. In all these cases we find minor variations of at most 0.03 in occupation numbers and Mulliken gross charges.

Polarization functions were included in the remaining five tests. The atomic occupations now vary within the following bounds:

$$N(\mathrm{H}) = 1.41 \ldots 1.46 \qquad \text{and} \qquad N(\mathrm{O}) = 9.55 \ldots 9.61$$

These variations have to be compared to the corresponding ones for the gross charges:

$$Q(\mathrm{H}) = 0.76 \ldots 0.85 \qquad \text{and} \qquad Q(\mathrm{O}) = 8.31 \ldots 8.50$$

which are significantly larger.

It is further instructive to consider the influence of polarization functions. The Mulliken gross charges change on inclusion of polarization functions from $Q(\mathrm{H}) \approx 0.63$ to $Q(\mathrm{H}) \approx 0.77$ and $Q(\mathrm{O}) \approx 8.75$ to $Q(\mathrm{O}) \approx 8.45$, whereas the occupation numbers change much less, from $N(\mathrm{H}) = 1.36$ to $N(\mathrm{H}) \approx 1.44$ and $N(\mathrm{O}) \approx 9.55$ to $N(\mathrm{O}) \approx 9.58$. The rather large change of atomic gross charges is internally inconsistent, since the corresponding gross

Table 1. Basis set dependence of population analysis for H_2O[a]

	H			O			
Basis[b]	N	R	Q	N	R	Q	ϵ
(84/42) (4/2)[c]	1.36	0.79	0.63	9.56	8.42	8.75	0.002
(84/42) (4/3)	1.36	0.79	0.63	9.55	8.41	8.74	0.002
(84/43) (4/3)	1.36	0.79	0.63	9.55	8.41	8.74	0.002
(95/53) (5/3)	1.36	0.79	0.61	9.54	8.40	8.77	0.002
(106/64) (5/3)	1.36	0.80	0.62	9.53	8.39	8.76	0.002
(84/42) (43)							
+ 1.35/0.8	1.44	0.82	0.76	9.57	8.36	8.48	0.007
1.35, 0.35/0.8	1.44	0.82	0.76	9.61	8.36	8.48	0.005
1.35/0.8, 0.2	1.41	0.81	0.85	9.57	8.36	8.31	0.018
(95/53) (5/3)							
1.26/0.63	1.46	0.83	0.75	9.58	8.33	8.50	0.006
1.35/0.8, 0.2	1.44	0.83	0.80	9.55	8.33	8.40	0.012

[a] Q denotes the gross charge, N and R denote atomic occupation and atomic charge as defined in Eqs. (17) and (26), ϵ = unassigned charge, Eq. (47), see also text.

[b] Contracted Huzinaga GTO basis [13], additional d sets on O and p sets on H are specified by orbital exponents η.

[c] The hydrogen basis was scaled by 1.2 in this computation.

charges of the polarization functions itself amount to 0.003 on H and 0.004 on O only. These small contributions consequently cannot explain the considerable variations of the Mulliken gross charge, which is an artifact of the MPA that does not reflect an electron shift of this magnitude. With this statement we only criticize the application of MPA to extended basis set computations for which it was not developed.

In Table 1 we have deliberately included some tests with quite unbalanced basis sets, and part of the variation of $N(\mathrm{H})$ and $N(\mathrm{O})$ is certainly due to changes in the density matrices investigated. One would expect, however, that addition of a second set of polarization functions on either O or H, compare lines 6–8 of Table 1, leads to minor changes in electron densities as is correctly indicated by the corresponding $N(\mathrm{H})$ and $N(\mathrm{O})$. Due to appreciable interatomic overlap integrals one may, of course, have more pronounced changes in the expansion coefficients of MOs in terms of the basis functions which leads to spurious changes in the Mulliken gross charges.

Since bonding in H_2O is dominantly covalent it appears reasonable to compute an atomic charge $R(\mathrm{A})$ according to Eq. (26). As $R(\mathrm{A})$ is derived from occupation numbers, it also shows no spurious changes.

4.2. *Population analysis for* N_2, CO, BF, Be_2

Table 2 gives the results of a population analysis for the above mentioned molecules in comparison with Davidson's analysis [8] of accurate HF-functions in terms of atomic HF-AOs. Our present results are in close agreement with those of Davidson, who has also demonstrated in an impressive way how occupation numbers may be used to discuss effects of chemical bonding. We therefore renounce on a detailed discussion and comment mainly on the small deviations (between Davidson's and the present results) which are due to the use of MAOs instead of HF-AOs as basis for the computation of occupation numbers.

Table 2. Results of population analysis for N_2, CO, BF, Be_2 [a]

		N^b	N	Q	$N_\pi{}^c$	$Q_\pi{}^c$	σ	$\sigma_\pi{}^c$	ϵ	ϵ^b
N_2		8.26	8.46	7.0	2.74	2.0	2.92	1.40	0.001	0.18
CO	C	7.15	6.85	5.60	1.48	0.87	2.18	1.18	0.001	0.16
	O	9.11	9.33	8.40	3.52	3.12				
BF	B	5.73	5.77	4.62	0.66	0.23	1.63	0.58	0.001	0.19
	F	9.58	9.86	9.38	3.92	3.76				
Be_2		–	3.97	4.0	–	–	−0.006	–	0.05	–

[a] For the meaning of N, Q, ϵ see Table 1 and text. A Huzinaga [13] (95/53) basis for first row atoms and (5/3) for hydrogen was augmented by a set of polarization functions. Number of MAOs is 5 for first row atoms and 1 for H. MAOs are expanded in the same basis as HF MOs.

[b] Ref. [8].

[c] Corresponding π contributions.

We first note that the unassigned charge ϵ is about two orders of magnitude smaller if MAOs are used instead of HF-AOs. This removes some uncertainties in the interpretation if electron shifts are in the same order as ϵ.

As the unassigned charge is now virtually zero we expect to get slightly larger values for $N(A)$, $N(B)$ and especially $N(A) + N(B)$. This is in fact the case for N_2. Since the MAOs are fitted to give the best possible description of the molecular density - and thus account for polarization effects - we also get a larger shared electron number σ of 2.9 *vs.* 2.68 obtained by Davidson.

For CO, however, the carbon occupation is smaller (6.85 *vs.* 7.15) for the MAOs than for SCF-AOs. This can be understood in the following way. The formation of CO is accompanied by a contraction of the $2p$ AOs of carbon caused by a slight electron transfer from C to O. This effect is e.g. reflected by the HF-orbital energies which are -0.43 for $2p$ of C and -0.56 for the π MOs of CO. $N(C)$ obtained from the HF-AOs is consequently larger than for the "contracted" MAOs fitted to describe the molecular density. A reverse effect occurs for the oxygen atom, of course. Quite the same explanation applies for $N(F)$ in BF which is 9.86 (MAOs) *vs.* 9.58 (HF-AOs).

A consideration of occupation numbers of BF is quite instructive. As $N(F) = 9.86$, the occupation numbers show that BF is largely ionic $B^{(+)}F^{(-)}$, since $N(F) = 10.0$ would only be possible if 5 MOs of BF can be written as pure fluorine AOs. The F^- charge cloud extends, however, into positions of large overlap with vacant B^+ orbitals which gives rather large $N(B)$ and $\sigma(BF)$. This conclusion is especially supported by the fact that the π contribution to σ, $\sigma_\pi = 0.58$, is virtually identical to the π occupation of boron, $N_\pi(B) = 0.66$.

Let us note that the shared electron densities decrease in the sequence N_2, CO, BF in agreement with the trend in bond strength. This decrease is mainly caused by decrease of the shared π-electron density (see also [8]).

In Table 2 we have also included a computation of Be_2 at $R = 5$ a.u. A set of two MAOs yields an unassigned charge $\epsilon = 0.05$, which is sufficiently small. The shared electron number is slightly negative, $\sigma = -0.006$, in agreement with the fact that no chemical bond is formed in Be_2. This confirms our considerations of Sect. 3 where the corresponding result of Roby [9] was discussed.

5. Summary

The difficulty of interpretation is probably the most unpleasant feature of accurate computations of molecular electronic wavefunctions. The molecular electron distribution and the effects of chemical bonding may be visualized in a qualitative way by plots of densities $\rho(\mathbf{r})$ or difference densities $\Delta\rho(\mathbf{r})$. A quantitative description of these effects requires a population analysis which necessarily suffers from its arbitrariness in defining atomic charges etc. Since this arbitrariness cannot be removed one should not try at all to describe a molecule by atomic charges only but consider a set of quantities - like occupation numbers and atomic charges - which then allows for a detailed discussion of chemical bonds.

In this paper we have extended earlier considerations of Davidson [8] and Roby [9]. Our approach may be summarized in the following way.

a) A set of MAOs is constructed for each atom. The MAOs are just slightly deformed HF-AOs, determined from the requirement that the MOs can be represented by the MAOs.
b) Compute the occupation numbers $N(\mathrm{A})$ of the space spanned by the orbitals associated with the corresponding atom A, and analogously the "atom pair occupation" $N(\mathrm{AB})$ etc., and further the shared electron number $\sigma(\mathrm{AB})$.
c) Discussion of molecular densities based on these quantities.
d) One can furthermore analyze the MAOs to discuss effects like orbital contraction (extension) and polarization.

This approach appears to have the following advantages:

a) The quantities $N(\mathrm{A})$, $N(\mathrm{AB})$ and $\sigma(\mathrm{AB})$ are virtually basis set independent.
b) Discussion of $N(\mathrm{A})$ and $\sigma(\mathrm{AB})$ allows for a reliable characterization of chemical bonds.
c) The qualities $N(\mathrm{A})$ and $\sigma(\mathrm{AB})$ fulfill the desired boundary conditions.

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Appendix: An Iterative Procedure to Determine MAOs

In order to maximize tr**DP** as a function of **P** by an iterative procedure we derive the first order variation of tr**DP**:

$$\begin{aligned}
\delta\,\mathrm{tr}\mathbf{DP} &= \mathrm{tr}\,\mathbf{D}\delta\mathbf{P} = \mathrm{tr}\,\mathbf{D}\delta\,[|\varphi\rangle\mathbf{S}^{-1}\langle\varphi|\,] = \\
&= \mathrm{tr}\,\{\mathbf{D}[\,|\delta\varphi\rangle\mathbf{S}^{-1}\langle\varphi| + |\varphi\rangle\mathbf{S}^{-1}\langle\delta\varphi| - |\varphi\rangle\mathbf{S}^{-1}(\delta\mathbf{S})\mathbf{S}^{-1}\langle\varphi|\,]\} \\
&= \mathrm{tr}\,\{[\mathbf{S}^{-1}\langle\varphi|\,\mathbf{D} - \mathbf{S}^{-1}\langle\varphi|\,\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1}\langle\varphi|\,]\,|\delta\varphi\rangle\} + \\
&+ \mathrm{tr}\,\{\langle\delta\varphi|\,[\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1} - |\varphi\rangle\mathbf{S}^{-1}\langle\varphi|\,\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1}]\} \\
&= \mathrm{tr}\,\{\mathbf{S}^{-1}\langle\varphi|\,\mathbf{D}(\mathbf{1}-\mathbf{P})\,|\delta\varphi\rangle\} + \mathrm{tr}\,\{\langle\delta\varphi|(\mathbf{1}-\mathbf{P})\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1}\} \\
&= 2\mathrm{tr}\,\{\mathbf{S}^{-1}\langle\varphi|\,\mathbf{D}(\mathbf{1}-\mathbf{P})\,|\delta\varphi\rangle
\end{aligned} \qquad \text{(A1)}$$

The last equality holds because tr**DP** is a real number.

We improve $|\varphi\rangle$ in a steepest ascent like manner:

$$|\varphi\rangle \rightarrow |\varphi\rangle + |\delta\varphi\rangle \qquad \text{(A2)}$$

with

$$|\delta\varphi\rangle = (\mathbf{1} - \mathbf{P})\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1} \tag{A3}$$

To maintain the "atomic" character of MAOs, $|\delta\varphi_A\rangle$ should only be represented by AOs centered on the same atom A, which is fulfilled if we project $|\delta\varphi_A\rangle$ onto the space spanned by the AOs of atom A by means of the projection operator $\tilde{\mathbf{P}}_A$

$$\tilde{\mathbf{P}}_A = |\mathbf{f}_A\rangle\mathbf{F}_A^{-1}\langle\mathbf{f}_A| \tag{A4}$$

We then get

$$|\varphi_A\rangle \rightarrow |\varphi_A\rangle + |\mathbf{f}_A\rangle\mathbf{F}_A^{-1}\langle\mathbf{f}_A|(\mathbf{1} - \mathbf{P})\mathbf{D}\,|\varphi\rangle\mathbf{S}^{-1} \tag{A5}$$

The replacement (A5) maintains the orthogonality constraint (10) in first order in $\delta\varphi_A$. A symmetric orthogonalization [14, 15] was performed to fulfil (10) exactly.

The convergency is about the same as in HF-computations.

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