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Population analysis based on occupation numbers II. Relationship between shared electron numbers and bond energies and characterization of hypervalent contributions

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The population analysis based on occupation numbers, originally proposed by Davidson, is briefly reviewed. A new way is proposed to determine modified AOs and to characterize hypervalent contributions. This is discussed in application to the molecules NSF, NSF_3, SF_6, OPCl, $OPCl_2$, O_2PCl, SO_2, ClO_4^-. It is the main objective of this work to investigate the connection between shared electron numbers σ - considered as a measure of covalent bond strength - and bond energies. σ is found to be a reliable measure of bond energies.

Key words: Population analysis — Bond energies — Hypervalency

1. Introduction

Methods of population analysis - first proposed by Mulliken [1] - are designed to relate molecular electronic structures to intuitive concepts of chemistry. For this purpose, one extracts from the wavefunction, which is usually of the SCF type, a small set of quantities such as bond orders and atomic charges for a shorthand description of the electronic structure. The problems of any such procedure - its ambiguity - are deeply rooted in the fundamental principles of Quantum Mechanics: bond orders and atomic charges are not observable and cannot be defined in a unique way. This is reflected by the often strong basis set dependence of results obtained, e.g. from a Mulliken population analysis (MPA).

An attractive alternative to the MPA has been introduced by Davidson for the case of diatomics [2]. He proposed to compute the occupation number N_A of

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Offprint requests to: C. Ehrhardt at the above address atom A in the molecule AB as

$$N_A = \text{tr } DP_A. \tag{1}$$

Here D denotes the molecular one particle density operator and P_A the projector onto the space of occupied SCF-AOs of atom A. For covalent bonds N_A is larger than the number of electrons of A but smaller than that of the corresponding rare gas atom. Davidson's idea allowed for the first time to quantify the intuitive concept that atoms forming chemical bonds tend to fill their valence shells by means of electron sharing. As a quantitative measure of electron sharing Davidson introduced

$$\sigma_{AB} = N_A + N_B - n_{AB} \tag{2}$$

where $n_{AB} = n_A + n_B$, is the number of electrons in the corresponding system. We will call σ_{AB} the shared electron number [3]. It is the main objective of the present paper to substantiate Davidson's claim that σ is a measure of bond strength (Sect. 5).
Davidson's ideas were generalized by Roby [4] to polyatomic molecules $ABC \ldots Z$. Let P_{XY}, P_{XYZ}, etc. denote the projectors onto the space spanned by the occupied SCF AOs of atoms X and Y, X and Y and Z, etc.

$$P_{XY\ldots} = \sum_{\mu} \sum_{\nu} |\mu\rangle (S^{-1})_{\mu\nu} \langle \nu|, \tag{3}$$

where μ, ν run over SCF-AOs of $X, Y, \ldots$. One then computes the occupations of pairs, triples, etc. of atoms as

$$N_{AB} = \text{tr } DP_{AB} \tag{4}$$

$$N_{ABC} = \text{tr } DP_{ABC}. \tag{5}$$

From these one furthermore gets the shared electron numbers, which Roby [4] unfortunately called "densities",

$$\sigma_{AB} = N_A + N_B - N_{AB} \tag{6}$$

$$\sigma_{ABC} = N_A + N_B + N_C - N_{AB} - N_{AC} - N_{BC} + N_{ABC}, \tag{7}$$

which are considered as measures of bond strength and of explicit three-body effects. The definition of σ_{AB}, σ_{ABC}, etc. is clearly related to simple considerations of the theory of sets, see Fig. 1, below. Roby's generalization of Davidson's ideas has been very useful, although other aspects of his work, such as a definition of atomic charges [4] and various "proofs", had a less fortunate fate [3].

The population analysis based on occupation numbers was further developed by Heinzmann and Ahlrichs [3] (HA). These authors proposed to consider

$$R_A = N_A - 1/2 \sum_{B \neq A} \sigma_{AB} + 1/3 \sum_{B > C (\neq A)} \sigma_{ABC} - \ldots \tag{8}$$

as a measure of electronic charge associated with atom A. The R_A fulfill the intuitively expected boundary conditions, e.g.

$$0 \leq R_A \leq 2m_A, \tag{9}$$

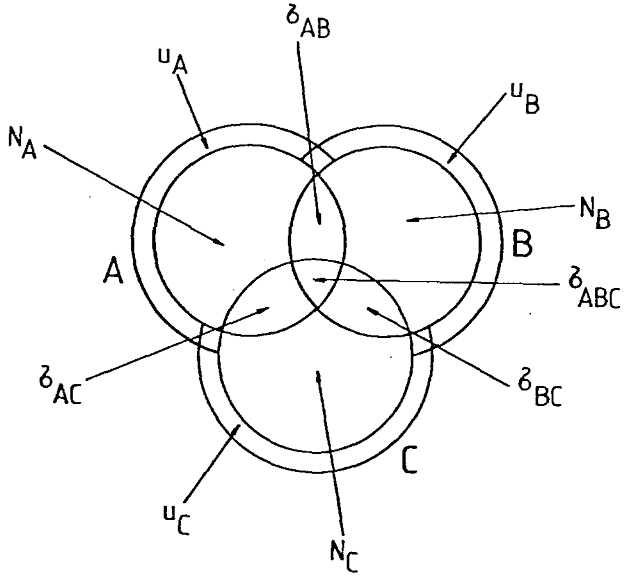

Fig. 1. Graphical representation of atomic occupation number N_A, shared electron number σ, and unshared population u

where m_A denotes the number of AOs on A considered in P_A. HA also demonstrated the remarkable stability and consistency of N_A, R_A, σ_{AB}, etc. for simple molecules even if rather unbalanced basis sets were employed.

At this stage, one has a method of population analysis provided the molecular SCF wave function can be represented by the occupied SCF-AOs. This is clearly not the case for extended basis set treatments for which an unassigned charge ε remains unaccounted for [2]

$$\varepsilon = n - \operatorname{tr} DP, \quad \varepsilon > 0, \tag{10}$$

where n denotes the number of electrons in the molecule and P the projector onto the space of SCF-AOs of all atoms. For diatomics ε is around 0.1 to 0.3 [2], which causes uncertainties in the interpretation. To cope with this problem, HA proposed to base the analysis on modified AOs (MAOs) instead of SCF-AOs. The MAOs were determined by the requirement that ε is minimized under the constraint that their atomic character is maintained [3].

There still remains a problem: in the above scheme one has to use a minimal number of AOs or MAOs per atom, otherwise results become meaningless [3]. This problem especially occurs for hypervalent compounds and will be discussed below.

Cruickshank and Avramides [5] (CA) made an interesting proposal to cope with this kind of problem. One keeps the number of AOs (or MAOs) minimal and uses the "unshared population" u_A as a measure for the polarization or hypervalent occupation

$$u_A = n - \operatorname{tr} DP_{A'B\ldots Z} \tag{11}$$

$P_{A'B...Z}$ projects onto the space spanned by the SCF-AOs (or MAOs) located on A and all basis functions on the remaining atoms $B \dots Z$, and n denotes again the number of electrons in the given molecule. As is obvious from the definition (11), the unshared population u_A can certainly not be attributed to any of the atoms $B \dots Z$, which justifies the term unshared population, as is depicted in Fig. 1.

In analogy to u_A one can define [5] u_{AB}, u_{ABC}, ... and quantities s_{AB} corresponding to σ_{AB}. These quantities can be used to decompose the unassigned charge ε and derive atomic charges which add up to the charge of the molecule [5]. Proceeding this way, one has at least formally solved the problem of unassigned charges.

In the present work we propose a new and simple way to determine MAOs, then incorporate ideas of CA [5] into the HA version of the population analysis based on occupation numbers to define hypervalent contributions. We finally demonstrate that the shared electron numbers σ indeed constitute a reliable measure of bond strength.

2. Determination of MAOs

Let us first recall that we use MAOs as a minimal set of AOs - we distinguish between AOs (orbitals from atomic SCF-calculations) or MAOs on one hand and basis functions on the other hand - which allow for a reliable description of extended basis set molecular SCF wavefunctions. After testing various possibilities, we have found that this goal can be achieved by simply diagonalizing the intraatomic part D_A of the molecular one-particle density D.

Let D be given in the usual basis set - denoted by f, g - expansion

$$D = \sum_{f,g} |f\rangle D_{fg} \langle g| \tag{12}$$

$$D_A = \sum_{f,g} |f\rangle D_{fg}^A \langle g| \tag{13}$$

$$D_{fg}^A = \begin{cases} D_{fg} & f \text{ and } g \text{ on } A \\ 0 & \text{else} \end{cases} \tag{14}$$

MAOs $|Aa\rangle$ are then obtained from

$$D_A |Aa\rangle = d_{Aa} |Aa\rangle, \tag{15}$$

where the atomic character of $|Aa\rangle$ is guaranteed through

$$|Aa\rangle = \sum_{f \in A} C_{Aa,f} |f\rangle. \tag{16}$$

This leads to the matrixeigenvalue problem, in an obvious notation,

$$D^A S^A C_{Aa} = d_{Aa} C_{Aa}. \tag{17}$$

From all solutions we select those MAOs with the largest occupation numbers with respect to the molecular density. The actual number of MAOs per atom is provided as input i.e. 1 for H, 5 for B to F, etc. This procedure is restricted to

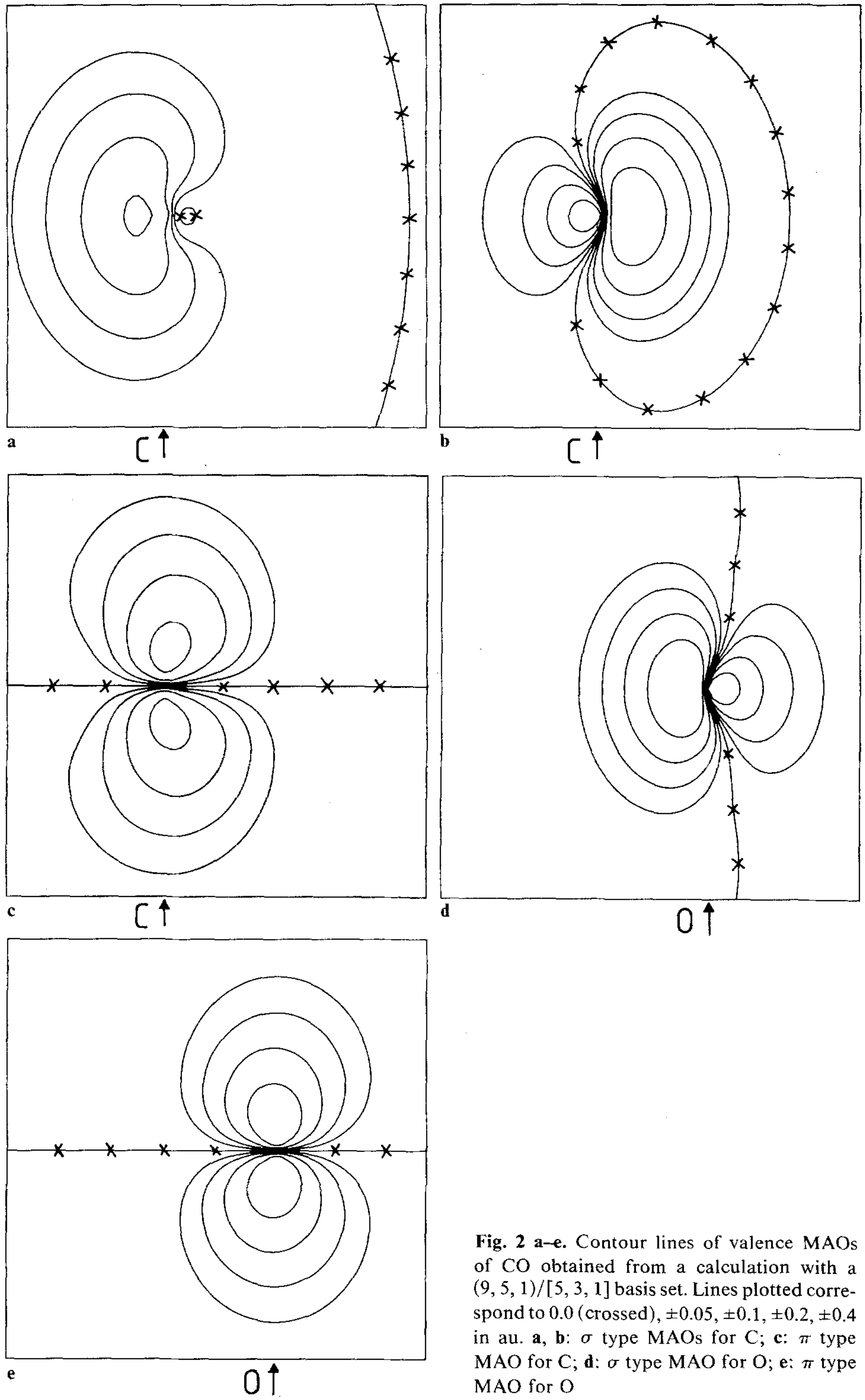

Fig. 2 a–e. Contour lines of valence MAOs of CO obtained from a calculation with a (9, 5, 1)/[5, 3, 1] basis set. Lines plotted correspond to 0.0 (crossed), ±0.05, ±0.1, ±0.2, ±0.4 in au. **a**, **b**: σ type MAOs for C; **c**: π type MAO for C; **d**: σ type MAO for O; **e**: π type MAO for O

LCAO-type treatments, since we tacitly assume atom centered basis functions, see Eqs. (13), (14), (16).

Since the molecular density operator D is totally symmetric - at least within the RHF method - and since MAOs are obtained as eigenfunctions of the intraatomic parts D_A, Eqs. (13)-(17), they transform according to the site group of the corresponding atom. This implies, e.g. $\sigma-\pi$ separation for linear molecules. However, the results of the present population analysis depend only on the space spanned by the MAOs of corresponding atoms, since N_A, N_{AB} and N_{ABC}, Eqs. (1), (4), (5), are invariant with respect to unitary transformations of MAOs of either atom.

In Fig. 2 are shown the contour diagrams of MAOs for the CO molecule in order to visualize some of the effects mentioned above. The π type MAOs are slightly polarized towards the bond region which results from the admixture of d_π contributions. The σ type MAOs are dominantly *sp* hybrids, the small d_σ contributions are not visible. The degree of hybridization - which does not affect the final results, as just mentioned - is stronger for C than for O. Since the 2*s* AO of oxygen is low lying it has an occupation close to 2.0, as for the 1*s* AO. This leads in fact to a rather strong mixture of 1*s* and 2*s* orbitals of oxygen within the present procedure to determine MAOs. Since the corresponding MAOs provide little information, their contour diagrams are not given in Fig. 2.

In Table 1 we report the unassigned charge ε for some simple molecules to document the sufficient smallness of ε for the present procedure. As can be seen from this Table, the values for ε are only slightly larger than those obtained by the optimization method of HA [3], but are significantly smaller than those of CA [5], although these authors used a small basis which did not include polarization functions. This clearly results from the fact that CA based their analysis on atomic SCF orbitals.

Another important test for the applicability of the present method is the basis set dependence of its results. This is not so easy to discuss, since it is difficult to

Table 1. Comparison of population analysis results for simple molecules[a]

	Q[b]			σ_{AB}[e]			ε[f]		
Molecule	CA[c]	HA[d]	This work	CA[c]	HA[d]	This work	CA[c]	HA[d]	This work
N_2	0.0	0.0	0.0	2.93	2.92	2.94	0.106	0.001	0.002
CO	0.07	0.24	0.06	2.59	2.18	2.57	0.105	0.001	0.002
CO_2	0.50	—	0.63	2.15	—	2.06	0.191	—	0.031
H_2O	−0.46	−0.33	−0.36	1.20	1.25	1.23	0.077	0.006	0.015

[a] Basis sets used: CA: H [3]; C, N, O [5, 3]; HA and this work: H [3, 1]; C, N, O [5, 3, 1]

[b] Charge of the central atom, for CO the charge of carbon evaluated from Eq. (19)

[c] Ref. [5]

[d] Ref. [3]

[e] Shared electron number, Eq. (6)

[f] Unassigned charge, Eq. (10)

distinguish between changes in the computed electronic structure (resulting from a change in the basis set used) and artefacts of the corresponding population analysis. For a consideration of electronic structures across a series of molecules one should always use - as is normally done - comparable and well-balanced basis sets, e.g. of DZP type. However, it is clearly desirable that the results of a population analysis do not crucially depend on the chosen basis set.

In Tables 2 and 3 the results of the present method for CO and NSF are compared with those of a Mulliken population analysis and the procedure of CA [5]. In these calculations we have deliberately employed quite unbalanced basis sets, such as a *d* set only for C or O in CO, Table 2. For both molecules, CO and NSF, the results of the present procedure are markedly more stable than those of the MPA, especially for quantities related to bond strengths, i.e. the SEN and the overlap charge. The Mulliken overlap charge in CO varies from 0.43 to 0.62 (44% change) whereas the SEN varies from 2.24 to 2.62 (17% change), Table 2. For NSF one even finds a negative SF overlap charge for the small basis set (−0.155, without *d* functions, Table 3), despite the fact that this basis leads to a pronounced minimum in the potential surface. The SEN for the NS bond changes from 1.845 (no *d* functions) to 2.184 for the large basis (2 *d*'s on all atoms), whereas the overlap charge more than doubles from 0.248 to 0.556. The atomic net charges Q_A computed with the present procedure also scatter much less than those of the MPA - by almost a factor of two - as is revealed by an inspection of Tables 2 and 3.

The results of the present method show a wider range of variations as those obtained by CA [5]. In the present authors' opinion the CA procedure appears to be too stable, i.e. it may underestimate the changes of electron distribution arising from a change in the basis set. The present method and the MPA always predict an increase of electronic charge on atom *A* if the basis set on *A* (and only on *A*) is enlarged. This trend is in line with the present authors' intuition: an increased flexibility of the basis of *A* should lead to a shift of electrons to this atom. A different trend is predicted by the procedure of CA: for NSF it is found that sulphur is depleted of electrons if a *d* set on S is added to the basis

Table 2. Results of the present and the Mulliken population analysis for CO for different basis sets

Basis	Q_c[a]	σ_{CO}[b](O_{CO})[c]	ε
(95/53), (95/53)	0.17 (0.33)	2.24 (0.46)	0.003
(951/531), (95/53)	0.053 (0.077)	2.59 (0.62)	0.002
(95/53), (951/531)	0.25 (0.46)	2.27 (0.43)	0.003
(951/531), (951/531)	0.057 (0.25)	2.57 (0.61)	0.002
(952/532), (952/532)	0.079 (0.29)	2.62 (0.62)	0.002

[a] Atomic charge, Eq. (19). The values of the Mulliken population analysis are given in parenthesis

[b] Shared electron number, Eq. (6)

[c] Mulliken overlap charge

Table 3. Comparison of MPA [1] and CA [5] population analysis of NSF with the present procedure

Basis	$Q_N{}^c$	$Q_S{}^c$	$Q_F{}^c$	$\sigma_{NS}{}^d(O_{NS})^e$	$\sigma_{SF}{}^d(O_{SF})^e$	ε^f
Without *d*-functions[a]	−0.479 (−0.477)	0.982 (1.015)	−0.503 (−0.538)	1.845 (0.248)	0.609 (−0.155)	0.036
Without *d*-functions[b]	−0.389 (−0.471)	0.837 (0.983)	−0.449 (−0.512)	—	—	—
1 *d*-set on S[a]	−0.318 (−0.202)	0.833 (0.634)	−0.515 (−0.433)	2.093 (0.503)	0.507 (0.012)	0.084
1 *d*-set on S[b]	−0.424 (−0.162)	0.875 (0.554)	−0.452 (−0.392)	—	—	—
1 *d*-set on N, S, F[a]	−0.408 (−0.332)	0.933 (0.788)	−0.525 (−0.456)	2.161 (0.556)	0.515 (0.013)	0.076
2 *d*-sets on N, S, F[a]	−0.488 (−0.454)	1.053 (0.957)	−0.565 (−0.502)	2.184 (0.556)	0.475 (0.012)	0.073
2 *d*-sets on N, S, F[b]	−0.467 (−0.539)	0.939 (1.047)	−0.472 (−0.508)	—	—	—

[a] This work

[b] Ref [5]. *s*, *p* basis sets used: 11*s*7*p* basis on S, 9*s*5*p* basis on N and F. Contraction in this work: [6, 4], [5, 3] in Ref. [5]: [7, 4], [4, 3]

[c] Atomic charge, Eq. (19). The values of the Mulliken population analysis are given in parenthesis

[d] Shared electron number, Eq. (6)

[e] Mulliken overlap charge

[f] Unassigned charge, Eq. (10)

without d functions (compare lines 2 and 4 in Table 3, the net charge Q_S increases from 0.837 to 0.875 on addition of $d(S)$).

3. Hypervalent contributions

Problems are encountered, however, in cases where the unassigned charge ε is relatively large, $\varepsilon \approx 0.2$. Since MAOs account for polarization effects of AOs involved in bonding - e.g. d_σ and/or d_π contributions in CO - this problem occurs mainly for so called hypervalent compounds. Typical examples are the highly symmetric molecules $SF_6(O_h)$, $ClO_4^-(T_d)$ or XeF_2 $(D_{\infty h})$, where occupied MOs of symmetry e_g, t_{2g} (SF_6), e (ClO_4^-) or $\pi_g(XeF_2)$ have no central atom s or p contributions and are stabilized by central atom d contributions, the familiar idea of backbonding. This stabilization effect is not well understood in detail - at least in our opinion. The corresponding MOs are mainly localized on ligand atoms and central atom d contributions are usually small: $c_d \lesssim 0.2$. One could, of course, simply increase the number of MAOs for atoms showing hypervalency, but results then become unreasonable [3].

Our efforts to incorporate effects of hypervalency into the present method of population analysis in a coherent and satisfactory way have not been entirely successful. It is possible, however, to make the problem explicit and provide at least a measure for the degree of hypervalency of corresponding atoms. For this purpose, we compute the unshared occupation [5] u_A, as defined in Eq. (11). Since our procedure is based on MAOs, the u_A clearly have a different meaning than in the work of CA [5]. In accordance with the above discussion we will call the u_A hypervalency occupations. As a justification we note that u_A can under no circumstances be associated with any other atom $B(\neq A)$, and that it measures the charge on A not accounted for by the (minimal number of) MAOs on A. For the simple cases SF_6, ClO_4^- and XeF_2 it is a matter of a straightforward analysis to show that u_A is virtually identical to the Mulliken net charge of corresponding d-functions. The range of u_A extends from $u_A \leq 0.001$ for atoms in normal valent compounds (N_2, CO) up to $u_A \approx 0.2$ for Cl in ClO_4^- or S in SF_6, which may be considered as cases showing rather pronounced hypervalent effects.

We further use the u_A for the computation of atomic charges. The R_A defined in Eq. (8) do not add up to the number of electrons n

$$\sum_A R_A = n - \varepsilon \tag{18}$$

as can be shown with the aid of Eqs. (8) and (10) [3]. Since the dominant contribution to ε are the hypervalency occupations u_A - which typically add up to 0.7ε - we employ the following equation to define atomic charges Q_A

$$Q_A = Z_A - R_A - u_A - \Delta, \tag{19}$$

which add up exactly to the total molecular charge if

$$\Delta = 1/m\left(\varepsilon - \sum_B u_B\right). \tag{20}$$

Here m denotes the number of atoms constituting the molecule. Eqs. (19) and (20) simply mean that one has distributed the deviation between $\sum_A (R_A + u_A)$ and n equally among the atoms. This appears to be justified since the correction term Δ is usually very small, typically $\Delta \approx 0.01$ electron.

4. Applications

Our procedure thus consists of the following steps:
(i) Determination of MAOs as eigenfunctions (with usually largest occupation numbers) of the intraatomic part of the density, Eqs. (12)-(17). The number of MAOs per atom is kept minimal and provided as an input parameter.

(ii) Computation of N_A, N_{AB}, N_{ABC}, according to Eqs. (1), (4), (5). From these quantities one immediately gets σ_{AB}, σ_{ABC} and R_A, Q_A, Eqs. (6-8), (19). The σ_{ABCD} are usually very small and are neglected.

(iii) We finally compute the u_A from Eq. (11).

The molecular electronic structure is then characterized by the Q_A, the charge associated with atom A, the shared electron number σ_{AB} as an indicator for the covalent bond strength, and the u_A which provide a measure for the hypervalency of atom A.

As demonstrative applications we report results for NSF, NSF_3, SF_6, $OPCl_3$, O_2PCl, SO_2 and ClO_4^- in Table 4. Let us first consider the u_A of the "hypervalent" atoms in these compounds. The u_A increase in the order (considered atom underlined) $O\underline{P}Cl < N\underline{S}F < O_2\underline{P}Cl \approx \underline{S}O_2 < O\underline{P}Cl_3 < N\underline{S}F_3 < \underline{S}F_6 < \underline{Cl}O_4^-$. This order is in agreement with (the authors') chemical intuition for the neutral molecules. The u_A are correlated with the charge on the central atom: removal of electrons lowers the energetic $p-d$ separation and enhances d participation.

Table 4. Results of the population analysis for hypervalent compounds

Molecule	Q[a]			σ[b]		$u_{S/P/CL}$[c]	ε[d]
NSF	N: −0.41	S: +0.93	F: −0.53	SN: 2.16	SF: 0.52	0.055	0.076
NSF_3	N: −0.67	S: +2.03	F: −0.45	SN: 2.14	SF: 0.56	0.144	0.222
SF_6		S: +2.67	F: −0.44		SF: 0.62	0.153	0.232
OPCl	O: −0.48	P: +0.78	Cl: −0.30	PO: 1.96	PCl: 0.84	0.047	0.064
$OPCl_3$	O: −0.70	P: +1.22	Cl: −0.18	PO: 1.53	PCl: 0.95	0.132	0.191
O_2PCl	O: −0.68	P: +1.50	Cl: −0.15	PO: 1.63	PCl: 1.02	0.101	0.163
SO_2		S: +1.29	O: −0.64		SO: 1.50	0.103	0.147
ClO_4^-	Cl: +2.40	O: −0.85		ClO: 1.02		0.196	0.286

[a] Atomic charge, Eq. (19)
[b] Shared electron number, Eq. (6)
[c] Hypervalency occupation, Eq. (11), for "central" atom
[d] Unassigned charge, Eq. (10)
basis sets: N, O, F: (9, 5, 1)/[5, 3, 1]
P, S, Cl: (11, 7, 1)/[6, 4, 1]

The u_A further depend on the properties of ligand atoms: hypervalency is enhanced by increases in $p_\pi - d_\pi$ interactions and the donor capability of the ligands as will be discussed below for $OPCl_3$ and O_2PCl. This is especially pronounced for ClO_4^-. Due to its negative charge ClO_4^- is a special case: anions have rather diffuse electron distributions (and small ionisation potentials) which are likely to lead to stronger interactions between ligand orbitals and central atom d functions. The large value $u_{CL} = 0.2$ in ClO_4^- is thus not surprising.

Let us next compare NSF with NSF_3. The NS-bond length as well as the SF-bond length are shorter in NSF_3 (2.676 au, 2.933 au) than in NSF (2.736 au, 3.105 au). The increase in the bond strength should be reflected by increased values of the shared electron numbers. As can be seen from Table 4, only σ_{SF} is slightly larger for NSF_3 while σ_{NS} is nearly the same for both compounds. The greater strength of the bonds in NSF_3 is partly due to the greater hypervalency contributions as expressed by the increased value of $u_S = 0.144$ (NSF_3) as compared to $u_S = 0.055$ (NSF). The ionic contributions to bonding are markedly larger in NSF_3 and cause additional stabilization.

Table 5. Correlation between shared electron numbers or Mulliken overlap populations and experimental bond energies ΔE^b

Molecule	σ[a]	O[b]	e[c]	ΔE^b [d] kJ/mol	$\delta(\sigma)$[e] kJ/mol	δ(O)[e] kJ/mol
H_2	1.46	0.42	0.500	436[f]	+30	−61
Li_2	1.17	0.36	0.196	101[g]	+2	−131
CH_4(C—H)	1.43	0.41	0.501	435[h]	+37	−54
C_2H_6(C—C)	1.39	0.34	0.501	367[h]	−17	−57
C_2H_4(C=C)	1.52/0.76	0.37/0.27	0.524/0.433	681[h]	+33	−9
C_2H_2(C≡C)	1.60/1.67	0.37/0.58	0.569/0.433	961[h]	+0.3	−17
N_2	2.94	0.72	0.568	941[i]	−37	+68
O_2	1.44	0.14	0.632	490[i]	−24	+228
F_2	0.60	0.041	0.730	158[h]	−68	+3
Na_2	1.21	0.36	0.182	75[f]	−19	−149
S_2	1.60	0.26	0.437	424[i]	+36	+113
Cl_2	0.86	0.083	0.507	242[k]	+17	+64

[a] Shared electron number, Eq. (6)
[b] Mulliken overlap charge
[c] Mean value for the orbital energy, Eq. (24). Values for σ, O and e are split into σ- and π-contributions
[d] Bond energies
[e] ΔE^b(exp) − ΔE^b(calc) for the present method $\delta(\sigma)$ and for a Mulliken population analysis δ(O)
[f] Ref. [8]
[g] Ref. [9]
[h] Ref. [10]
[i] Ref. [11]
[k] Ref. [12]

basis sets: H: (5, 1)/[3, 1]
Li: (7, 1)/[4, 1]
C−F: (9, 5, 1)/[5, 3, 1]
Na: (11, 7)/[6, 4]
S, Cl: (11, 7, 1)/[6, 4, 1]

The molecules OPCl and O_2PCl have recently been investigated by Schnöckel et al. [6] and are compared in Table 4 with the well known $OPCl_3$. OPCl is a normal valent compound with a polar PO double bond, as is shown by $\sigma_{PO} = 1.96$ ($\sigma \approx 2.2$ for covalent double bonds, see Table 5) and the charges on P and O. The PO double bond character is less pronounced in O_2PCl ($\sigma_{PO} = 1.63$) and $OPCl_3$ ($\sigma_{PO} = 1.53$). Oxygen is more effective in withdrawing charge than 2Cl: the charge on P is larger in O_2PCl ($Q_P = 1.50$) than in $OPCl_3$ ($Q_P = 1.22$). The increased charges on P and O in O_2PCl and $OPCl_3$, as compared to OPCl, indicate a stabilization of PO bonds by ionic contributions. Experimental data indicate the PCl force constant to be larger in O_2PCl than $OPCl_3$. This is in line with the results of the population analysis since σ_{PCl} decreases from 1.02 to 0.95 and ionic contributions (as measured by Q_P, Q_{Cl}) are slightly smaller in $OPCl_3$. In $OPCl_3$ we find a larger u_P than in O_2PCl (0.132 vs. 0.101), although the charge Q_P is larger in O_2PCl (1.50 vs. 1.22 in $OPCl_3$). This indicates - as expected - that Cl is a better π-donor and that $p_\pi - d_\pi$ interactions are more favorable for P-Cl than for P-O as a consequence of the better agreement in size of corresponding AOs.

The above examples show how the present method can give quantitative values for the increase of bond strengths by hypervalency.

5. The relationship between shared electron numbers σ and bond strength

Based on more intuitive reasonings Davidson [2] has concluded that σ_{AB} is a measure of the saturation or inertness of a chemical bond. σ_{AB} should, therefore, be related to the covalent bond strength which in turn is clearly related to bond energies ΔE^b_{AB}. It is tempting to investigate the correlation between σ_{AB} and ΔE^b_{AB} in covalent compounds. The ΔE^b_{AB} are here assumed to add up to the total atomization energy of the molecule and are identical to the bond dissociation energy for diatomics. Since σ_{AB} is a pure number and ΔE^b_{AB} clearly an energy such a comparison requires a conversion factor. This idea is at the heart of all basic discussions of the origin of chemical binding: ΔE^b_{AB} is (positively) correlated with the overlap of AOs - or the σ_{AB}, both pure numbers - and with the ionization potential (IP) e_A of atom A in question, see e.g. Ref. [7] for an up to date discussion. As an example we just mention the Wolfsberg-Helmholtz approximation, which yields for a homonuclear diatomic electron pair bond

$$\Delta E^b = 2\beta = K \cdot e_A \cdot S \tag{21}$$

where S denotes the overlap integral, e_A the IP and K a proportionality constant.

The simplest possible relationship between σ_{AB} and ΔE^b_{AB}, the corresponding bond energy, is therefore of the form

$$\Delta E^b_{AB} = \alpha \frac{e_A + e_B}{2} \sigma_{AB} + \beta \tag{22}$$

with parameters α and β, the latter of which should be close to zero.

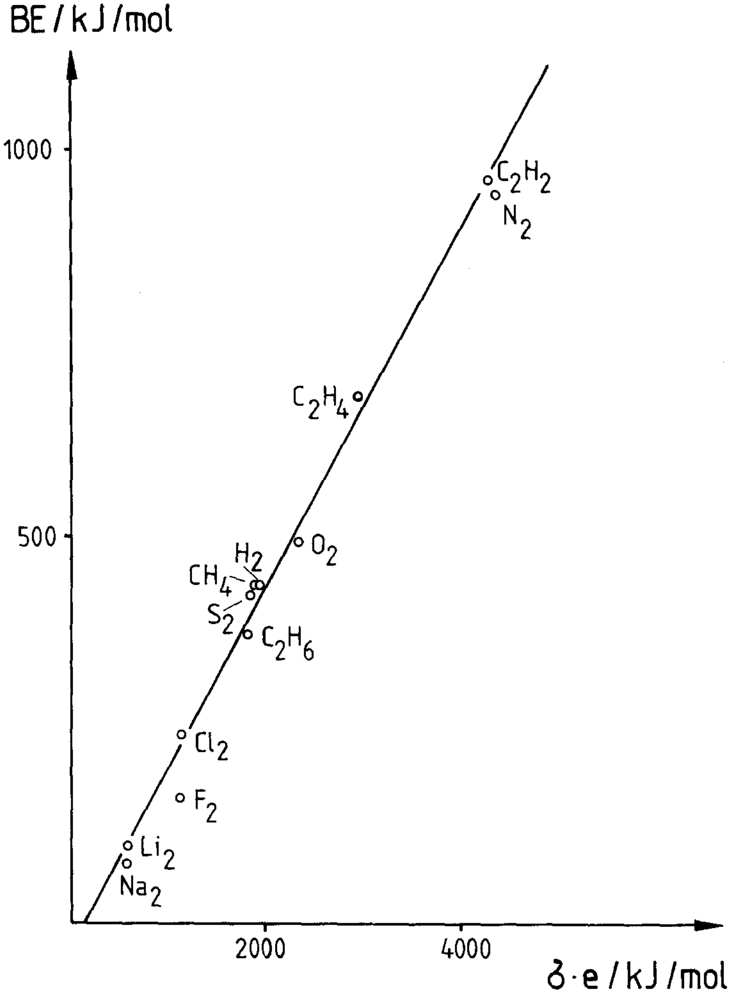

Fig. 3. The relationship between bond energies ΔE^b and the product of shared electron numbers and atomic SCF orbital energies $\sigma \cdot e$, as explained in the text

We have checked (22) by means of a regression analysis. For simplicity we have inserted for e_A, e_B the atomic SCF orbital energy of the corresponding valence AO. This is uniquely defined for molecules like N_2, O_2, F_2, S_2, Cl_2 or H_2, Li_2, Na_2 where bonding dominantly involves p or s valence AOs. For hydrocarbons the situation is slightly more complicated since hybridization is of importance in these cases. Since the shared electron numbers can be broken into σ and π contributions for C_2H_4 and C_2H_2, and since the hybridization of σ-orbitals is sp^2 and sp, or sp^3 for CH_4, it appears near at hand to put for these cases

$$\Delta E^b_{AB} = \alpha\left[\sigma^{(\sigma)}_{AB}\frac{e^{sp^n}_A + e^{sp^n}_B}{2} + \sigma^{(\pi)}_{AB}\frac{e^{\pi}_A + e^{\pi}_B}{2}\right] + \beta, \qquad (23)$$

with

$$e_A(sp^n) = \frac{n \cdot e_A(P) + e_A(S)}{n+1} \tag{24}$$

in an obvious notation.

A similar correlation as the one lined out above can be investigated with σ_{AB} replaced by the Mulliken overlap charge O_{AB}.

The input data for the regression analysis and the results are collected in Table 5 and yield the following values for α and β in Eq. (22):

$$\alpha = 0.23$$

$$\beta = -41.0 \text{ kJ/mol}$$

with a correlation coefficient 0.994 (see Fig. 2).

The correlation between σ_{AB} and bond strengths, as expressed by the corresponding ΔE^b_{AB}, is in fact surprisingly accurate: the relationship (22) allows for a prediction of bond energies (on the basis of SCF results) with a mean deviation of only 26.7 kJ/mol for weakest (F_2, Na_2) to strongest bonds (N_2, $C\equiv C$). The only appreciable deviation occurs for F_2 where (22) is in error by 68 kJ/mol. We further note that the correlation between overlap charges O_{AB} and ΔE^b_{AB} is less pronounced - though still satisfactory - than that between σ_{AB} and ΔE^b_{AB}. We consider this result as a convincing confirmation of the ideas originally put forward by Davidson as described in his pioneering paper [2].

6. Summary

We have considered the population analysis based on occupation numbers proposed by Davidson [2] and Roby [4] in using modified atomic orbitals (MAO) as suggested by Heinzmann and Ahlrichs [3]. A new and simple way to determine MAOs has been introduced and tested in applications, Sect. 2. In Sect. 5 it has been demonstrated that shared electron numbers σ are closely correlated to bond energies and thus constitute a reliable measure of (covalent) bond strength. We further proposed to consider the unshared population u_A as defined by Cruickshank and Avramides [5] as a measure for hypervalency, Sect. 3.

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