Theor Chim Acta 68:221-229 (1985)

THEORETICA CHIMICA ACTA

Classical chemical concepts from *ab initio* SCF calculations

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(Received January 18, revised May 5, 1985)

Alternative definitions of bond order, valency, gross orbital populations and total atomic charge for SCF wavefunctions are compared. It is found that there are sound theoretical and numerical reasons for preferring definitions based on the Löwdin density matrix.

Key words: Valency — Bond order — Atomic charge — Orbital population — Mulliken analysis — Löwdin analysis

1. Introduction

There has been a revival of interest recently in the classical chemical concepts of e.g. bond order, atomic valency, atomic charge etc. for molecular systems and how the results of *ab initio* quantum chemical calculations can be related to such concepts. Various definitions have been proposed (and reproposed) in the literature for certain of these quantities for SCF wavefunctions in terms of the usual density and overlap matrices, most recently by Mayer [1, 2] and Natiello and Medrano [3]. Mayer's definitions for bond order and valency are based on the "standard" density matrix, whilst those of Natiello and Medrano on the density matrix in the Löwdin orthogonalized basis.

Although there does not appear on a first inspection to be any *a priori* reason to prefer one definition to another, as Mayer has stated [4], it might be considered somewhat unsatisfactory to have different definitions for the same quantities. The purpose of this paper is to compare via numerical calculations results from the two alternative definitions for bond order and atomic valency, and also gross orbital occupancy and total atomic charge, and to show that indeed there are sound reasons, both numerical and theoretical, for preferring the definitions based on the Löwdin density matrix.

2. Theoretical considerations

Mayer's definition for the bond order between two atoms A, B in a molecule is [1]

$$B_{AB} = \sum_{i\in A} \sum_{j\in B} (\boldsymbol{PS})_{ij}(\boldsymbol{PS})_{ji} \tag{1}$$

where the sum is over all basis functions i, j belonging to atoms A and B respectively. $\boldsymbol{S}$ is the usual overlap matrix in the AO basis and $\boldsymbol{P}$ the "density matrix", which in the closed-shell case takes the form

$$\boldsymbol{P} = 2 \sum_{i=1}^{\mathrm{occ}} \boldsymbol{C}_i \boldsymbol{C}_i^{+} \tag{2}$$

where $\boldsymbol{C}_k$ is the column vector formed by the LCAO coefficients of the kth occupied MO.

The alternative definition of Natiello and Medrano is [3]

$$B_{AB} = \sum_{i\in A} \sum_{j\in B} (\boldsymbol{S}^{1/2}\boldsymbol{PS}^{1/2})^2_{ij} \tag{3}$$

which is the same as (1) with the matrix $\boldsymbol{PS}$ replaced by $\boldsymbol{S}^{1/2}\boldsymbol{PS}^{1/2}$, the Löwdin "density matrix". Since this matrix is symmetric (3) can be written as a square. The valency of an atom A in a closed-shell system is given in both cases by

$$V_A = \sum_{B(B\neq A)} B_{AB}. \tag{4}$$

What properties do we require for our bond orders and valencies? For a system such as methane (CH_4) we would hope to reproduce as closely as possible the classical valencies of 4 for carbon, 1 for hydrogen and a C–H bond order of unity. Classically, the bond order between the individual hydrogen atoms is zero; however we can admit the possibility of (slight) interactions between the hydrogens and consider a small positive bond order to indicate a degree of attraction whilst a small negative value would suggest repulsion. From this consideration alone one would tend to prefer Mayer's definition (1) since with (3) *all* bond orders would be positive.

Turning to gross orbital occupancy and total atomic charge, these are normally determined from a standard Mulliken population analysis [5]. The spinless electron density can be written in terms of the $\boldsymbol{P}$ matrix and the basis orbitals $\{\Phi_k\}$ as [6]

$$p_1(r) = \sum_{ij} \boldsymbol{P}_{ij}\Phi_i(r)\Phi_j^*(r). \tag{5}$$

Integrating the electron density over all space must give N, the total number of electrons in the system, and so

$$\int p_1(r)\,\mathrm{d}r = \sum_{ij} \boldsymbol{P}_{ij}\boldsymbol{S}_{ij} = N. \tag{6}$$

Defining normalized orbital and overlap populations

$$q_i = \boldsymbol{P}_{ii}, \qquad q_{ij} = \boldsymbol{P}_{ij}\boldsymbol{S}_{ij},$$

then (6) can be written as

$$\sum_i q_i + \sum_{ij(i \neq j)} q_{ij} = N. \tag{7}$$

The charge is thus divided out into an amount q_i arising from each net orbital population and q_{ij} from each overlap population. The gross orbital occupancy for orbital ϕ_i is then

$$g_i = q_i + \sum_{j(j \neq i)} q_{ij} \tag{8}$$

and the total charge on atom A

$$C_{\mathrm{A}} = \sum_{i \in \mathrm{A}} g_i. \tag{9}$$

Now ideally the gross orbital occupancy for a given orbital should never be less than zero (no electrons in the orbital) or greater than 2 (doubly occupied). For an open shell (UHF) system, where α and β orbitals are considered separately, g_i should not exceed 1. Mulliken himself noted in one of his original papers [5] that slight deviations from ideality did occur, the reasons for which were obscure. In point of fact cases can be found for which these slight deviations are so large as to produce virtually meaningless results. This is particularly so if diffuse functions (frequently associated with near linear dependency) are included in the basis, which is often done with e.g. negative ions. The only invariant in the analysis is equation (7) i.e. no matter how you distribute the charge it must add up to N.

Consider now the Löwdin density matrix $\boldsymbol{P}' = \boldsymbol{S}^{1/2}\boldsymbol{P}\boldsymbol{S}^{1/2}$. The diagonal elements of this matrix have the interesting properties that [7]

$$\mathrm{Tr}\,\boldsymbol{P}' = \sum_i \boldsymbol{P}'_{ii} = N \tag{10}$$

and

$$\begin{aligned} &0 \leq \boldsymbol{P}'_{ii} \leq 2, && && \text{closed shell} \\ &0 \leq \boldsymbol{P}'^{\alpha}_{ii} \leq 1, && 0 \leq \boldsymbol{P}'^{\beta}_{ii} \leq 1, && \text{open shell.} \end{aligned} \tag{11}$$

Equation (10) is the counterpart of (7) and Eqs. (11) are exactly the properties we require for our gross orbital occupancies. Thus we can define

$$\begin{aligned} g_i &= \boldsymbol{P}'_{ii} \\ C_{\mathrm{A}} &= \sum_{i \in A} \boldsymbol{P}'_{ii}. \end{aligned} \tag{12}$$

From a theoretical viewpoint therefore one might be tempted to prefer definition (1) for the bond order since we can get more information out of the system than with (3), which does not admit the possibility of unfavourable interactions between atoms in the same molecule, whereas for gross orbital occupancies definition (12) seems much more suitable than (8) which can give rise to unreasonable orbital occupancies. However it should perhaps be noted at this point that Mayer's definitions for bond order and the standard Mulliken population analysis are intimately related [1], and therefore one might expect that situations in which the Mulliken analysis breaks down may also lead to a corresponding breakdown in bond order. In the next section we examine how the alternative definitions perform in practice.

3. Numerical results

Tables 1 and 2 show calculated atomic charges, valencies and bond orders for a variety of small closed-shell molecular systems with various basis sets obtained using the "Mulliken" and "Löwdin" analyses respectively. All calculations were done on a VAX 11/750 using the Gaussian 82 program package [8] modified accordingly (only a Mulliken population analysis is normally available). In most cases either experimental geometries or geometries optimized for the basis set chosen were used.

Comparing the two tables it would seem that, on the whole, the Löwdin analysis performs better. The atomic charges are in most cases intuitively more reasonable

Table 1. Atomic charges, valencies and bond orders using the "Mulliken" analysis

System	Basis	Atom	Charge	Valency	Bond orders	
H_2CO	STO-3G	C	5.94	3.91	C–O	2.03
		O	8.19	2.11	C–H	0.94
		H	0.94	0.96	O–H	0.041
					H–H	0.014
CH_4	6-31G*	C	6.66	3.85	C–H	0.96
		H	0.83	0.93	H–H	−0.010
H_2O	6-31G**	O	8.67	1.76	O–H	0.88
		H	0.66	0.88	H–H	−0.002
CH_3^+	6-31G*	C	6.08	2.57	C–H	0.86
		H	0.64	0.85	H–H	−0.003
CH_3^-	6-31G*	C	6.83	2.89	C–H	0.96
		H	1.06	0.93	H–H	−0.015
CH_3OH	3-21G	C	6.27	3.61	C–O	0.87
		O	8.68	1.72	C–Hc	0.91
		Hc	0.82	0.91	C–Hc′	0.92
		Hc′	0.78	0.91	O–H	0.82
		H	0.63	0.83		
CH_2OH_2[a]	3-21G	C	6.45	2.18	C–O	0.31
		O	8.67	1.88	C–Hc	0.93
		Hc	0.87	0.93	O–H	0.78
		H	0.57	0.79		

[a] ylid. staggered C_s symmetry, with long (1.868 Å) C–O bond. C_s plane bisects the $\widehat{HCH}$ and $\widehat{HOH}$ angles

Table 2. Atomic charges, valencies and bond orders using the "Löwdin" analysis

System	Basis	Atom	Charge	Valency	Bond orders
H_2CO	STO-3G	C	5.93	3.97	C-O 2.05
		O	8.12	2.13	C-H 0.96
		H	0.98	1.00	O-H 0.038
					H-H 0.003
CH_4	6-31G*	C	6.64	3.90	C-H 0.97
		H	0.84	0.99	H-H 0.006
H_2O	6-31G**	O	8.45	2.06	O-H 1.03
		H	0.77	1.05	H-H 0.025
CH_3^+[a]	6-31G*	C	5.72	2.82	C-H 0.94
		H	0.76	0.96	H-H 0.011
CH_3^-	6-31G*	C	6.99	3.03	C-H 1.01
		H	1.00	1.02	H-H 0.006
CH_3OH	3-21G	C	6.06	4.01	C-O 1.08
		O	8.40	2.10	C-Hc 0.97
		Hc	0.94	1.02	C-Hc′ 0.97
		Hc′	0.91	1.01	O-H 0.94
		H	0.76	0.97	
CH_2OH_2	3-21G	C	6.34	2.54	C-O 0.49
		O	8.30	2.36	C-Hc 1.01
		Hc	0.96	1.03	O-H 0.92
		H	0.72	0.95	

[a] There was a slight loss of symmetry for CH_3^+ i.e. the hydrogens became nonequivalent in the Löwdin analysis. This was restored by using 5 pure *d* functions instead of 6 cartesians for the carbon *d* orbitals

Table 3. Atomic charges on oxygen and carbon with a 3-21G basis set

	Atomic charge	
System	Mulliken	Löwdin
H_2O^+	8.13	7.78
H_2O	8.73	8.47
H_2O^-	8.73	8.71
$C_2H_2^+$	6.00	5.75
C_2H_2	6.34	6.15
$C_2H_2^-$	6.30	6.34

and the valencies and bond orders are normally closer to the classical values than their Mulliken counterparts. For example the CH_3^- ion corresponds almost exactly to the classical description of three C-H single bonds with the extra electron located in a lone-pair on carbon. Further evidence for better charge distributions with the Löwdin analysis is given in Table 3 which shows charges on oxygen in H_2O^+, H_2O and H_2O^- and on carbon in $C_2H_2^+$, C_2H_2 and $C_2H_2^-$ at the 3-21 G level. Again the Löwdin values look the more likely. Finally Tables 4–6 demonstrate that the traditional Mulliken analysis can go badly wrong. Results

Table 4. Gross orbital occupancies for the $C_3H_3^-$ ion with 3-21G and 3-21+G basis sets

		3-21G Populations		3-21+G Populations	
Atom	Orbital	Mulliken	Löwdin	Mulliken	Löwdin
C1	1*S*	1.9876	1.9794	1.9882	1.9785
	2*S*	0.3860	0.4347	0.3904	0.4217
	2*PX*	0.5625	0.5481	0.5556	0.5278
	2*PY*	0.5947	0.5761	0.5981	0.5726
	2*PZ*	0.3415	0.3332	0.3494	0.3303
	3*S*	0.9931	0.6967	1.0639	0.5753
	3*PX*	0.7246	0.7871	0.6388	0.6847
	3*PY*	0.3885	0.6003	0.2934	0.5325
	3*PZ*	0.5199	0.5593	0.4604	0.4931
	dS			2.2012	0.1362
	dPX			0.0955	0.1294
	dPY			−0.2322	0.0857
	dPZ			0.0426	0.0955
C2	1*S*	1.9874	1.9794	1.9883	1.9792
	2*S*	0.4400	0.4369	0.4427	0.4372
	2*PX*	0.3348	0.3135	0.3394	0.3133
	2*PY*	0.7183	0.6779	0.7246	0.6856
	2*PZ*	0.4768	0.4655	0.4632	0.4427
	3*S*	0.7399	0.5420	0.7513	0.4709
	3*PX*	0.4688	0.5089	0.4469	0.4437
	3*PY*	0.3398	0.5286	0.2856	0.5003
	3*PZ*	0.6627	0.6411	0.6045	0.5618
	dS			−0.6419	0.0971
	dPX			0.0078	0.0786
	dPY			−1.9809	0.1207
	dPZ			0.1004	0.0830
C3	1*S*	1.9862	1.9758	1.9870	1.9759
	2*S*	0.3648	0.3872	0.3707	0.3875
	2*PX*	0.5631	0.5768	0.5264	0.5198
	2*PY*	0.5558	0.5239	0.5652	0.5333
	2*PZ*	0.5070	0.4651	0.5271	0.4879
	3*S*	0.9048	0.5643	0.9651	0.5063
	3*PX*	0.9371	0.9085	0.7932	0.7763
	3*PY*	0.3171	0.5314	0.3027	0.4965
	3*PZ*	0.4730	0.5728	0.5245	0.5486
	dS			0.8886	0.0935
	dPX			0.1998	0.1841
	dPY			−0.1154	0.0672
	dPZ			0.0209	0.0692
H4	1*S*	0.4668	0.4619	0.4671	0.4494
	2*S*	0.4555	0.5005	0.3743	0.4044
H5	1*S*	0.4732	0.4734	0.4728	0.4586
	2*S*	0.4279	0.4882	0.3400	0.4029
H6	1*S*	0.4732	0.4734	0.4728	0.4586
	2*S*	0.4279	0.4882	0.3400	0.4029

Table 5. Bond orders for the $C_3H_3^-$ ion with 3-21G and 3-21+G basis sets

	3-21G Basis		3-21+G Basis	
Bond order	Mulliken	Löwdin	Mulliken	Löwdin
C1-C2	2.30	2.39	−4.26	2.52
C2-C3	1.57	1.68	−0.01	1.75
C1-C3	0.11	0.20	−1.76	0.28
C1-H4	0.94	0.94	1.25	0.88
C3-H5	0.95	0.95	1.15	0.90
C3-H6	0.95	0.95	1.15	0.90

Table 6. Atomic charges and valencies for the $C_3H_3^-$ ion with 3-21G and 3-21+G basis sets

	3-21G Basis				3-21+G Basis			
	Mulliken		Löwdin		Mulliken		Löwdin	
Atom	Charge	Valency	Charge	Valency	Charge	Valency	Charge	Valency
C1	6.50	3.39	6.51	3.60	8.45	−4.86	6.56	3.75
C2	6.17	3.82	6.09	4.17	3.53	−4.87	6.21	4.44
C3	6.61	3.62	6.51	3.81	7.56	0.49	6.65	3.88
H4	0.92	0.95	0.96	1.02	0.84	0.93	0.85	0.99
H5	0.90	0.95	0.96	1.02	0.81	0.93	0.86	0.99
H6	0.90	0.95	0.96	1.02	0.81	0.93	0.86	0.99

are shown for one possible structure of the $C_3H_3^-$ ion (Fig. 1) with two basis sets, 3-21G and 3-21+G. The latter basis includes diffuse *S* and *P* functions on carbon. There are no dramatic differences between the two approaches at the 3-21G level; the gross orbital populations are all positive and less than 2 in the Mulliken analysis which is nice to see. One might frown upon the Löwdin valency of the central carbon being greater than 4, but this could perhaps be taken as an indication of C–C–C conjugation. The picture at the 3-21+G level is completely different. The presence of diffuse orbitals has had a disastrous effect on the Mulliken analysis, with gross orbital populations in excess of 2 and ludicrous negative populations (including −1.98 for the diffuse P_y function on the central carbon!). The breakdown is total: the calculated atomic charges are clearly not realistic and the predicted valencies for carbon of −4.9 and 0.5 are absurd. The fact that Mayer's definition (1) permits negative bond orders might not be such a good idea after all. The Löwdin analysis on the other hand gives results similar to those at the 3-21G level, the diffuse functions having no noticeable adverse effect.

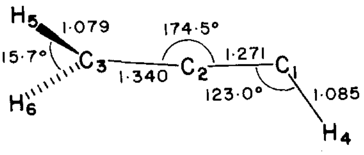

Fig. 1. Geometrical parameters for $C_3H_3^-$ ion (C_s symmetry)

Why should the presence of diffuse functions have such dire consequences for the Mulliken analysis? The answer lies in the form of the SCF MO's, which often have very large coefficients when diffuse orbitals are included in the basis. This results in correspondingly large $\boldsymbol{P}$ matrix elements. Such large matrix elements are not present in the Löwdin density matrix $\boldsymbol{P}'$, since these are removed by correspondingly small terms in the $\boldsymbol{S}^{1/2}$ matrix (diffuse functions giving near zero eigenvalues for the overlap matrix $\boldsymbol{S}$).

4. Discussion and conclusions

The results and considerations of the previous sections would clearly seem to suggest that it is more appropriate to define the quantities discussed here i.e. bond order, valency, gross orbital occupancy and atomic charge via the Löwdin Density matrix ($\boldsymbol{P}'$) than with the "standard" $\boldsymbol{P}$ matrix in the non-orthogonal basis. However one should recall that, as noted by Mayer [4], by performing a Löwdin orthogonalization the form of the basis orbitals is changed and they will no longer possess purely "atomic" character. Thus when comparing the gross orbital occupancies of Table 4, it should be borne in mind that whereas the Mulliken populations refer to the original basis AO's, the Löwdin populations refer to their orthogonalized counterparts. This point was also mentioned by Natiello and Medrano in Ref. [9], and is to be considered further in their Ref. [6] (not yet published at the time of writing).

These considerations aside, the Löwdin analysis appears to perform better and is certainly more stable—surely a "vaguely atomic" orbital with a gross occupancy of 0.12 electrons is preferable to a well defined AO with occupancy −1.98.

Finally, a brief comment on the interpretation of the calculated quantities. Atomic charge and orbital populations are more or less self-explanatory; bond order and valency are more difficult to interpret rigorously. It is tempting to assume that e.g. the larger the value for a bond order, the stronger the bond, all other things being equal. However, this is an oversimplification, since the *form* of the orbitals is also an important factor [6], and conclusions about the nature of chemical bonds based on formal bond orders alone should be treated with caution.

Only qualitative differences should be looked for in any case; for example, whilst it is reasonable to conclude that the C-O bond in CH_2OH_2 is weaker than that in CH_3OH (see Tables 1, 2), the small differences between the C-H bond orders in CH_3OH and H_2CO are of little significance.

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