Theoret. chim. Acta (Berl.) 31, 63—73 (1973)

A New Definition of Atomic Charges in Molecules*

Karl Jug

Institut für Theoretische Chemie der Universität Stuttgart and Department of Chemistry,
Saint Louis University Saint Louis, Missouri 63156, USA**

Received April 9, 1973

A new definition of atomic charges in molecules is presented which conserves charge and dipole moment. It contains the Mulliken and Löwdin definitions as special cases of zero and first order truncations of commutator expansions. The definition allows for a systematic improvement of charges paralleling the improvement of the basis set in the LCAO approximation. We have tested the definition in thirteen selected diatomics and polyatomics in optimal minimal Slater basis set SCF calculations by means of 4G-level Gaussian expansions. The results suggest that the proposed definition is better than either Mulliken's or Löwdin's definition.

Key words: Atomic charges – Dipole moments.

1. Introduction

In recent years, many attempts have been made to improve the standard population analysis suggested by Mulliken [1] and also by Daudel [2]. They fall essentially in three categories:

i) The partitioning of two-center atomic orbital overlap integrals in atomic parts. The Mulliken definition falls in this category. More sophisticated definitions are those by Löwdin [3], which conserves the dipole moment of a two-center charge distribution and by Christoffersen [4], which uses coefficients of an SCF calculation for weighting.

ii) The use of symmetrically orthogonalized atomic orbitals [5]. This method is essentially underlying the CNDO and related methods by Pople [6].

iii) The definition of regions in space which are attributed exclusively to atoms. This method has been pursued qualitatively by means of force fields by Bader [7] and quantitatively through considerations of noninteracting atoms in molecules by Politzer [8].

The advantages of these methods are largely set off by their disadvantages. The third category is most attractive to the experimental chemist and it also offers theoretically a broader range of application than either the first or the second. In particular, the latter ones cannot be directly applied to single-center orbital sets. In a case of single-center MO's with one non-linear variation parameter, Hartmann and Jug [9] segmented the space in atomic regions for five-membered heterocyclic systems to obtain atomic charges. The problem was here as

---

* Presented in part at the E. U. Condon Symposium, Sanibel Island, Florida, 21–27 January 1973.

** Permanent address.

well as in the other methods of this category [7, 8] the definition of the atomic regions and the integration. In general, this problem is of crucial difficulty and the latter methods have been applied so far to linear systems only. The advantage of the second method is that no overlap distributions appear explicitly. Implicitly it needs atomic orbitals from other centers to obtain orthogonalized AO's. No justification has been given so far with regard to the relevance of these admixtures. The first category seems to offer the least difficulty if an atomic basis set is used and consequences of partitioning are investigated properly. This means that a relation to a measurable physical quantity has to be established. Only the Löwdin definition based on the conservation of the dipole moment is of this type.

In previous papers [10, 11] we have laid the ground work for a general definition of the first category and applied the concept to several diatomics. The application was limited to four-orbital expansions of integrals related through commutator equations. This paper extends the application to optimal minimal basis set expansions for thirteen selected diatomics and polyatomics. It also gives proof of the conservation of charge and dipole moment in a general fashion. Tables with atomic net charges, $\sigma-\pi$ separation, atomic occupation numbers, dipole moments and ionic character of bonds are illustrating the differences between Mulliken, Löwdin and this work's definition of atomic charges.

2. The Method

The commutator equation

$$u=[t,x] \tag{2.1}$$

with hermitian and antihermitian operators t, x and u is equivalent to an infinite expansion of integrals over the above operators in a complete basis set χ

$$u_{\mu\nu}=\sum_{\chi,\chi'} t_{\mu\chi}(S^{-1})_{\chi\chi'}x_{\chi'\nu}-x_{\mu\chi}(S^{-1})_{\chi\chi'}t_{\chi'\nu} \tag{2.2}$$

with

$$u_{\mu\nu}=\langle\mu|u|\nu\rangle \quad \text{etc.}$$

In truncated expansions the above relationship between the integrals in (2.2) is in general only approximately valid.

In the following, we discuss two cases for which (2.2) is representing an equality in a *finite* expansion.

1. Conservation of charge: $u=0$, $x=1$.

If we take as expansion functions χ, χ' only those which are used to define the inverse matrix S^{-1}, it holds that

$$\begin{aligned}\sum_{\chi,\chi'}^{N} t_{\mu\chi}(S^{-1})_{\chi\chi'}S_{\chi'\nu}-S_{\mu\chi}(S^{-1})_{\chi\chi'}t_{\chi'\nu}\\ =\sum_{\chi}^{N} t_{\mu\chi}\delta_{\chi\nu}-\sum_{\chi'}\delta_{\mu\chi'}t_{\chi'\nu}\\ =t_{\mu\nu}-t_{\mu\nu}\\ =0\,.\end{aligned} \tag{2.3}$$

2. Conservation of dipole moment: $u = 0$, $x = \boldsymbol{r}$, $t = \boldsymbol{r}$

$$\sum_{\chi,\chi'}^{N} \boldsymbol{r}_{\mu\chi}(S^{-1})_{\chi\chi'}\boldsymbol{r}_{\chi'\nu} - \boldsymbol{r}_{\mu\chi}(S^{-1})_{\chi\chi'}\boldsymbol{r}_{\chi'\nu} = 0\,. \tag{2.4}$$

The first case demonstrates that charge is conserved no matter what operator is chosen for t. For the conservation of the dipole moment $t = \boldsymbol{r}$ is necessary. Combining these two observations we choose $t = \boldsymbol{r}$ for the charge distribution in order to have it on the same footing as the dipole moment partitioning. This means that the total dipole moment of a distribution càn be represented as the sum of a charge transfer moment and hybrid atomic moments. We now write (2.2) in such a way that the purpose of partitioning is more apparent. Consider two orbitals μ and ν on two different atomic centers A and B. We rewrite (2.2) for $u = 0$ and $t = \boldsymbol{r}$ by using only orbitals on centers A and B in the expansion

$$x_{\mu\nu} = \frac{Q_{\mu\nu}}{Q_{\mu\nu}^2}\left[\sum_{\mu'}^{\mathrm{A}} F_{\mu'\nu}x_{\mu\mu'} - \sum_{\nu'}^{\mathrm{B}} F_{\nu'\mu}x_{\nu'\nu} + \sum_{\nu'\neq\nu}^{\mathrm{B}} F_{\nu'\nu}x_{\mu\nu'} - \sum_{\mu'\neq\mu}^{\mathrm{A}} F_{\mu'\mu}x_{\mu'\nu}\right] \tag{2.5}$$

with

$$F_{\mu\nu} = \sum_{\chi}(S^{-1})_{\mu\chi}\boldsymbol{r}_{\chi\nu}$$

$$Q_{\mu\nu} = F_{\mu\mu} - F_{\nu\nu}\,.$$

Equation (2.5) presents a two-center integral $x_{\mu\nu}$ in terms of single-center distributions $x_{\mu\mu'}$ and $x_{\nu\nu'}$ on atoms A and B plus additional two-center terms $x_{\mu\nu'}$ and $x_{\mu'\nu}$. If we expand these latter terms again in terms of single-center distributions we can iteratively obtain a representation of any two-center term of x by single-center terms of atoms A and B. Since we have already proved that for $x = 1$ and $x = \boldsymbol{r}$ we obtain equalities (2.3) and (2.4), it means that in (2.5) we distribute two-center overlap integrals among atoms A and B under conservation of charge and dipole moment. In any polyatomic molecule we define a charge transfer in the direction of an internuclear axis. This corresponds to the dipole moment conservation in this direction. In such a local coordinate system there are no two-center integrals perpendicular to the internuclear axis which would need expansion. If partitioning is defined in a local coordinate system and the unitary transformation to molecular coordinate systems performed properly [6], the rotational invariance is guaranteed. The translational invariance is a simple consequence of (2.5) and (2.3). The two-center terms of any other physical quantity x, which commutes with the dipole moment, can be partitioned iteratively in single-center distributions according to (2.5). Such other quantities are the quadrupole moment and higher moments. However, their expansion is exact only in an infinite complete set; finite expansions will in general lead only to approximations for $x_{\mu\nu}$.

In the following charge and dipole moment analysis of SCF MO calculations, we now use in (2.5) *all* atomic orbitals μ' and ν' of the SCF basis set instead of four (or less) orbitals previously [11]. We found the four-orbital expansions rather too short. Their results were often close to Löwdin's two-orbital expansions $\mu' = \mu$ and $\nu' = \nu$.

3. Calculations and Discussion

We have performed SCF calculations with optimal minimal Slater basis sets expanded in Gaussians on the 4G-level. The program used was MOLPRO written by Meyer and Pulay. The following thirteen molecules were investigated: CO, LiF, LiH, BH, HF, H_2O, NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, HCCLi, HCCF. Geometries for the diatomics were taken from Ransil [12], for H_2O from del Bene and Pople [13], for NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2 from Palke and Lipscomb [14] and HCCLi, HCCF from McLean and Yoshimine [15]. In the latter two cases the HC distance chosen was the same as in C_2H_2. The exponents for LiH, BH, HF were from Ransil [12], all others from Pople and coworkers [16].

Atomic net charges were calculated for these molecules according to Mulliken, Löwdin and our method in Section 2. These net charges are defined as the differences between gross atomic populations and nuclear charges. The results are presented in Table 1. In compounds containing hydrogen, the Mulliken

Table 1. Atomic net charges

Molecule	Atom	Mulliken	Löwdin	This work
CO	C	+0.220	+0.245	+0.284
	O	−0.220	−0.245	−0.284
LiF	Li	+0.262	+0.340	+0.257
	F	−0.262	−0.340	−0.257
LiH	Li	+0.347	+0.618	+0.459
	H	−0.347	−0.618	−0.459
BH	B	+0.019	+0.304	+0.153
	H	−0.019	−0.304	−0.153
HF	F	−0.234	−0.060	−0.196
	H	+0.234	+0.060	+0.196
H_2O	O	−0.400	−0.010	−0.300
	H	+0.200	+0.005	+0.150
NH_3	N	−0.492	+0.158	−0.362
	H	+0.164	−0.053	+0.121
CH_4	C	−0.080	+0.788	+0.056
	H	+0.020	−0.197	−0.014
C_2H_6	C	−0.045	+0.597	+0.072
	H	+0.015	−0.199	−0.024
C_2H_4	C	−0.160	+0.276	−0.078
	H	+0.080	−0.138	+0.039
C_2H_2	C	−0.198	−0.005	−0.173
	H	+0.198	+0.005	+0.173
HCCLi	H	+0.165	−0.037	+0.132
	C	−0.273	−0.116	−0.293
	C	−0.187	−0.248	−0.165
	Li	+0.295	+0.401	+0.326
HCCF	H	+0.207	+0.020	+0.187
	C	−0.217	+0.002	−0.163
	C	+0.082	−0.016	−0.008
	F	−0.072	−0.006	−0.016

analysis leaves the hydrogen more positive by an average amount of 0.035 charge units than our method, except LiH and BH where the relative shift is 0.11 and 0.13. The Löwdin method yields much larger shifts towards hydrogen ranging from 0.17–0.28. The Mulliken analysis disqualifies itself on the basis of non-conservation of the dipole moment of charge distributions. Alternatively, if the two-center atomic dipole moments would be partitioned on the same footing as the charge, the Mulliken analysis would yield atomic hybrid moments on hydrogen, an intolerable situation since there is only a $1s_H$-orbital in the basis set. The relative shift of charge towards hydrogen in our method is particularly important in CH_4 and C_2H_6 where the polarity is reversed compared to Mulliken. Since a long time, the organic chemists considered hydrogen as slightly negative in CH_4. Wheland [17] reasoned that the electronegativity difference of C and H would be overcompensated by the relative effect of size of the C and H atoms in covalent bonds and hybrid moments would also tend to generate a bond dipole moment in which the C is at the positive end. The Löwdin definition is apparently overshooting the corrective effect of charge transfer to hydrogen. It is chemically not appealing to find H to be strongly negative (0.20) in CH_4, fairly negative (0.05) in NH_3 and almost neutral (0.005) in H_2O. The explanation is that the Löwdin method corrects the Mulliken method in the right direction, however, its expansion of (2.5) is too short for the stringent condition of dipole moment conservation. The shift of charge towards hydrogen is also strongly pronounced in a method by Politzer and Harris [8]. They applied their method to *standard double-zeta* calculations of C_2H_2, HCCLi and HCCF. They find a much stronger shift of charge compared to Mulliken for all the atoms than we do with *optimal minimal* basis set calculations. Unfortunately there is no reference to implications for the dipole moment in their work.

For CO and LiF, the differences between Mulliken's, Löwdin's and this work's method are not so pronounced as in most of the other molecules. How relevant the absolute values of these net charges are will be discussed in relation to dipole moments and quality of wavefunctions in one of the following paragraphs.

Table 2 illustrates a breakdown of charge transfer in terms of σ and π separation. From this table it appears that the σ electrons are polarized in the nuclear framework and the π electrons then adjust in the field of nuclei *and* σ electrons. Thus they are creating an opposite trend compared to the σ electrons. The three types of charge definitions differ only in the magnitude of σ polarization and π adjustment. It should also be pointed out that in minimal basis sets, π-charges are the same in Löwdin's and our method since there is only one π orbital on each atom available for expansion. The second π orbital on any atom cannot be coupled by the dipole operator to any one of the first set.

Table 3 contains the orbital occupation numbers. Most significant for a comparison is the fact that Löwdin's definition strongly depopulates the p-orbital in the direction of an X–H bond in compounds containing hydrogen when compared with the Mulliken approximation. Our definition reduces this effect considerably. An explanation for the huge transfer by the Löwdin method is given if we consider the center of charge of a $1s_H 2_{pX}$ distribution. Since the p-orbital is directed towards atom H, the center of charge is moved towards H;

Table 2. $\sigma-\pi$ net charge separation

Molecule	Atom		Mulliken	Löwdin	This work
CO	C	σ	+0.360	+0.324	+0.363
		π	−0.140	−0.079	−0.079
	O	σ	−0.360	−0.324	−0.363
		π	+0.140	+0.079	+0.079
LiF	Li	σ	+0.830	+0.800	+0.717
		π	−0.568	−0.460	−0.460
	F	σ	−0.830	−0.800	−0.717
		π	+0.568	+0.460	+0.460
HCCLi	H	σ	+0.165	−0.037	+0.132
		π	0	0	0
	C	σ	−0.235	−0.066	−0.243
		π	−0.038	−0.050	−0.050
	C	σ	−0.379	−0.410	−0.327
		π	+0.192	+0.162	+0.162
	Li	σ	+0.449	+0.513	+0.438
		π	−0.154	−0.112	−0.112
HCCF	H	σ	+0.207	+0.020	+0.187
		π	0	0	0
	C	σ	−0.123	+0.098	−0.067
		π	−0.094	−0.096	−0.096
	C	σ	+0.150	+0.040	+0.048
		π	−0.068	−0.056	−0.056
	F	σ	−0.234	−0.158	−0.168
		π	+0.162	+0.152	+0.152

this means a distribution favoring hydrogen. The difference in populations for the three methods is much smaller for the 2*s*-orbital. Except for the diatomic hydrides and H_2O both Löwdin's and our definition increase the population of the 2*s*-orbital compared to Mulliken's and thus generate an opposite effect to the 2*p*-shift.

Table 4 shows the various parts of the dipole moment in our charge definition. In CO the total hybrid moment is slightly larger than the charge moment and of opposite direction. In essence the atomic moment of the C atom is responsible for the sign of the total dipole moment. The sign of the dipole moment of the wavefunction agrees with the experimental moment [18]. The agreement of magnitude, however, is fortunate since we know that the SCF limit yields the wrong sign [19]. Since the CI results are most often insufficient for good agreement with experiment, it appears at this point rather useless to attempt an analysis with an improved wavefunction. This statement does not hold for LiF. The optimized minimal basis function of LiF yields only 53% of the large experimental dipole moment. Hence, it appears to underestimate the charge moment considerably. Also the relative magnitudes of charge and hybrid moments cannot be considered as final. This also means that the absolute value of net charge in LiF is still greatly underestimated by the best minimal basis set. In all other cases where experimental values are known the wavefunction generates an agreeable dipole moment.

Table 3. Atomic occupation numbers

Molecule	Atom	1*s*	2*s*	2*px*	2*py*	2*pz*	
CO	C	1.998	1.671	0.570	0.570	0.971	Mulliken
		1.990	1.714	0.539	0.539	0.972	Löwdin
		1.987	1.706	0.539	0.539	0.944	This work
	O	1.999	1.857	1.430	1.430	1.504	
		1.995	1.868	1.461	1.461	1.461	
		1.993	1.883	1.461	1.461	1.486	
LiF	Li	1.991	0.090	0.284	0.284	0.089	
		1.986	0.108	0.230	0.230	0.106	
		1.983	0.167	0.230	0.230	0.132	
	F	1.999	1.940	1.716	1.716	1.891	
		1.997	1.972	1.770	1.770	1.831	
		1.998	1.954	1.770	1.770	1.765	
LiH	Li	1.994	0.402	0	0	0.258	
		1.981	0.293	0	0	0.107	
		1.976	0.392	0	0	0.173	
	H	1.347					
		1.618					
		1.459					
BH	B	1.999	1.809	0	0	1.173	
		1.996	1.811	0	0	0.889	
		1.995	1.807	0	0	1.045	
	H	1.019					
		1.304					
		1.153					
HF	F	1.999	1.946	2	2	1.288	
		1.999	1.934	2	2	1.127	
		1.999	1.918	2	2	1.278	
	H	0.766					
		0.940					
		0.804					
H_2O	O	1.998	1.862	1.108	2	1.432	
		1.997	1.855	0.887	2	1.270	
		1.997	1.841	1.063	2	1.399	
	H	0.800					
		0.995					
		0.850					
NH_3	N	1.997	1.597	1.068	1.068	1.762	
		1.988	1.604	0.793	0.793	1.664	
		1.985	1.663	0.990	0.990	1.735	
	H	0.836					
		1.053					
		0.879					
CH_4	C	1.994	1.141	0.982	0.982	0.982	
		1.973	1.143	0.699	0.699	0.699	
		1.965	1.294	0.895	0.895	0.895	
	H	0.980					
		1.197					
		1.014					

Table 3 (continued)

Molecule	Atom	1*s*	2*s*	2*px*	2*py*	2*pz*
C_2H_6	C	1.994	1.151	0.974	0.974	0.953
		1.974	1.184	0.693	0.693	0.860
		1.967	1.295	0.886	0.886	0.894
	H	0.985				
		1.199				
		1.024				
C_2H_4	C	1.995	1.162	1.015	1	0.989
		1.974	1.207	0.704	1	0.838
		1.966	1.314	0.905	1	0.893
	H	0.920				
		1.138				
		0.961				
C_2H_2	C	1.997	1.130	1	1	1.071
		1.971	1.197	1	1	0.837
		1.961	1.282	1	1	0.930
	H	0.802				
		0.995				
		0.827				
HCCLi	H	0.835				
		1.037				
		0.868				
	C	1.997	1.161	1.019	1.019	1.076
		1.972	1.243	1.025	1.025	0.852
		1.962	1.329	1.025	1.025	0.953
	C	1.996	1.304	0.904	0.904	1.080
		1.973	1.534	0.919	0.919	0.904
		1.965	1.486	0.919	0.919	0.875
	Li	1.991	0.307	0.077	0.077	0.253
		1.982	0.294	0.056	0.056	0.211
		1.978	0.361	0.056	0.056	0.222
HCCF	H	0.793				
		0.980				
		0.813				
	C	1.996	1.092	1.047	1.047	1.034
		1.971	1.141	1.048	1.048	0.789
		1.960	1.229	1.048	1.048	0.877
	C	1.997	1.010	1.034	1.034	0.844
		1.973	1.166	1.028	1.028	0.822
		1.963	1.192	1.028	1.028	0.797
	F	1.999	1.933	1.919	1.919	1.302
		1.999	1.901	1.924	1.924	1.258
		1.998	1.907	1.924	1.924	1.264

In LiH, FH, NH_3, HCCLi and HCCF the charge moment dominates greatly over the hybrid moment, in H_2O they are almost equal and in BH the hybrid moment is considerably larger and of opposite sign to the hybrid moment.

Table 4. Dipole moment partitioning (a.u.)

Molecule	Charge	Hybrid			Total[a]	Exp.[b]
		X_1	X_2	X_3		
CO	−0.605	0.956	−0.312		0.039	0.044
LiF	−0.732	−0.542	−0.101		−1.375	−2.60
LiH	−1.382	−0.941			−2.323	−2.31
BH	−0.357	0.984			0.627	—
FH	0.339	0.233			0.572	0.715
OH_2	0.381	0.361			0.742	0.706
NH_3	0.452	0.261			0.713	0.578
HCCLi	1.256	0.029	−0.469	1.075	1.891	—
HCCF	−0.471	0.249	0.221	−0.261	−0.262	−0.279[c]

[a] Positive entry means − + polarity for the molecule as written.

[b] McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman and Co. 1963.

[c] Reference from Yoshimine, M., McLean, A. D.: Internat. J. Quantum Chem. 1S, 313 (1967).

Table 5. Partial ionic character of atoms in molecules (%)

Molecule	Electronegativity[a]	Dipole moment[b]	This work[c]
CO	66	2	28
LiF	89	91	26
LiH	26	77	46
BH	< 1	45	15
HF	59	41	20
H_2O	39	33	15
NH_3	19	27	12
CH_4	4	—	1
C_2H_6	4	—	2
C_2H_4	4	—	4
C_2H_2	4	—	17

[a] Pauling, L.: The nature of the chemical bond, p. 64, 70. Ithaca, N. J.: Cornell University Press 1948.

[b] Ibid, p. 46.

[c] Charge.

Finally Table 5 summarizes our charge results and compares them with popular definitions by Pauling based on electronegativity differences and experimental dipole moments. We find as Bader and Hanneker [7] did qualitatively that electronegativity is not too reliable to assess the ionic character of an atom in a molecule. Total experimental dipole moments are also limited since we can only estimate or measure by infrared spectroscopy *bond* dipole moments in molecules with vanishing total moments. Bond dipole moments however, are mostly not additive. A weak point in our work is the net charge of LiF which we would expect to be at least as ionic as LiH.

4. Conclusion

The method tested in this paper for atomic charges in molecules is most general and useful in an LCAO SCF approach. It reveals that great differences in charges appear between Mulliken's and Löwdin's definition. The results we obtain by expansions larger than in either of the above methods lie often in between these extremes. To assess the reliability of the suggested method more thoroughly we are in the process of calculating quadrupole moments to see how well the charge definition conserves the quadrupole moment. In principle we know that our method will reproduce a multipole moment with any desired degree of accuracy if we enlarge the basis set for the SCF calculation. This means it is on the same footing as the LCAO approach itself and suffers its drawbacks. An imbalanced basis set might yield a poor charge if the total dipole moment is far off the experimental value. LiF represents such a case. We plan to investigate this molecule with a double zeta set. It should be mentioned also that the convergence of our iterative charge process depends on the main single-center terms of (2.5). Convergence was fast in the hydrides, medium in CO, HCCLi, HCCF and slow in LiF. This seems to indicate somehow the quality of the wavefunction with respect to dipole moments. A question in this context is: Would similar basis sets yield similar charges. This question was asked and partially answered by Politzer and Mulliken [20]. In our definition we would like to tentatively state this: If two wavefunctions yield similar virial quotients and dipole moments and their density distribution in space is similar, we expect similar charges. We shall investigate this point more thoroughly. Finally it should be mentioned that a charge definition based on a least square fit of two-center distributions in single-center distributions is pursued by Meyer [21]. This idea has been used also by Newton [22] and Billingsley and Bloor [23] for integral approximations rather than charges. The method does not conserve the total dipole moment and the charge has to be renormalized. It would be interesting to see how large the difference in charges is between the least square method and our method.

Acknowledgement. The main part of this work was done at the Theoretical Chemistry Institute of the University of Stuttgart. I appreciated the hospitality of Prof. H. Preuss and his staff during my stay. Discussions about the topic of this paper with Prof. H. Preuss and Dr. W. Meyer have greatly helped to advance the project. Computer time from the University of Stuttgart and Saint Louis University is gratefully acknowledged. Dr. Meyer was helpful in furnishing his program MOLPRO for the SCF calculations.

References

1. Mulliken, R. S.: J. Chem. Phys. **23**, 1833 (1955)
2. Daudel, R., Laforgue, A.: C.R. seances Acad. Sci. Paris **233**, 623 (1951)
3. Löwdin, P. O.: J. Chem. Phys. **21**, 374 (1953)
4. Christoffersen, R. E., Baker, K. A.: Chem. Phys. Letters **8**, 4 (1971)
5. Löwdin, P. O.: J. Chem. Phys. **18**, 365 (1950)
6. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
7. Bader, R. F. W., Hanneker, W. H.: J. Am. Chem. Soc. **88**, 280 (1966)
8. Politzer, P., Harris, R. R.: J. Am. Chem. Soc. **92**, 6451 (1970)

9. Hartmann, H., Jug, K.: Theoret. Chim. Acta (Berl.) **3** (1965)
10. Jug, K.: Theoret. Chim. Acta (Berl.) **26**, 231 (1972)
11. Jug, K.: Theoret. Chim. Acta (Berl.) **29**, 9 (1973)
12. Ransil, B.: Rev. Mod. Phys. **32**, 245 (1960)
13. del Bene, J., Pople, J. A.: Chem. Phys. Letters **4**, 426 (1969)
14. Palke, W. E., Lipscomb, W.: J. Am. Chem. Soc. **88**, 2384 (1966)
15. McLean, A. D., Yoshimine, M.: Tables of linear molecular wavefunctions, IBM 1967
16. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
17. Wheland, G. W.: Resonance in organic chemistry, p. 204ff. New York: Wiley 1955
18. McLean, A. D., Yoshimine, M.: J. Chem. Phys. **45**, 3467 (1966)
19. Schaefer, III, H. F.: The electronic structure of atoms and molecules, p. 196ff. Reading: Addison-Wesley 1972
20. Politzer, P., Mulliken, R. S.: J. Chem. Phys. **55**, 5135 (1971)
21. Meyer, W.: Private communication
22. Newton, M. D.: J. Chem. Phys. **51**, 3917 (1969)
23. Billingsley, F. P., Bloor, J. E.: J. Chem. Phys. **55**, 5178 (1971)

Prof. Dr. K. Jug
Department of Chemistry
Saint Louis University
Saint Louis, Missouri 63156, USA