Theoret. Chim. Acta (Berl.) 39, 301–312 (1975)

Charge Distributions and Multipole Moments in Molecules

Karl Jug
Theoretische Chemie, Technische Universität Hannover

Received January 6, 1975/May 30, 1975

The consideration of multipole moments is suggested as a new criterion for the validity of assignments of atomic charges in molecules. The total quadrupole and octupole moments generated by our definition of atomic charges are compared with the exact moments of the underlying wavefunction for various basis sets in selected diatomics. The analysis includes also total overlap and total dipole moment partitioning as well as 1σ MO overlap partitioning. All considerations together allow us to assess the validity of our charge definition as compared to Mulliken's and Löwdin's and the quality of the basis set.

Key words: Atomic charges – Multipole moments

1. Introduction

Population analyses for an assignment of atomic charges in molecules are based on 1) overlap partitioning between the two atoms involved, 2) space partitioning between all the atoms of a molecule, 3) zero overlap between properly defined orthogonal atomic orbitals. Recently [1], we proposed a new definition for such an assignment which falls in the first category. Therefore it is particularly suited for the LCAO formalism. We tested our method with optimal minimal basis set SCF calculations on thirteen selected diatomics and polyatomics and compared the results with those of the Mulliken [2] and Löwdin [3] definition which are of the same category. The emphasis at that time was on dipole moments. Any assignment of point charges to the atoms creates a molecular dipole moment, in the following called the charge moment, and any assignment of a point charge center off the atoms creates an atomic dipole moment, called a hybrid moment. We asked the question of how well these point moments are in agreement with the moments calculated directly with the underlying SCF wavefunction. We could show that the Mulliken definition of charge assignment does not conserve the dipole moment of individual overlap integrals, but the overall effect is often buried in internal shifts of moments which are difficult to trace. Moreover, the Löwdin definition conserves all dipole moments over atomic orbitals in much the same way as our method does. To obtain a more complete view of the situation we introduce here an analysis of multipole moments connected with the atomic charges. This serves also as a new criterion for the consistency of a charge definition. For this purpose linear molecules are particularly suitable because of their preference axis. Charge transfer can be considered along the internuclear axis. How this transfer affects the quadrupole and octupole moment components of this direction is investigated. Basis sets of varying size and quality including some close to Hartree-Fock limit were tested for LiF and FH, typifying ionic and covalent bonds. In addition to total charges and moments, overlap and dipole moment partitioning among the two atoms are presented, to have a more complete idea about the differences between the three methods. It also seemed worthwhile to present the atomic charges resulting from the lowest lying 1σ MO's since the Mulliken analysis had resulted in values below zero in some cases. Optimal minimal basis set calculations on LiH, BH and CO serve to show the general trend.

2. The Method

The method is based on a reduction of two-center integrals via an expansion in terms of one-center integrals. We used commutator equations between approximate hermitian operators to obtain expansion coefficients. The operators considered are 1. the identity operator to characterize the charge, 2. one component of the position vector for the dipole moment, 3. higher powers of the component just mentioned for multiple moment components. The dipole operator serves to obtain the coefficients in an overlap expansion, i.e. it generates the weighting factors f for distribution among single-center terms:

$$S_{\mu\nu}=\sum_{\mu'} f_{\mu'} S_{\mu\mu'}+\sum_{\nu} f_{\nu'} S_{\nu\nu'}$$

It turns out that the Mulliken and Löwdin definition can be considered as special cases of such an expansion truncated at zero or first order. Whereas these methods retain only a restricted number of orbitals in the expansion our method includes all basis functions of the two atoms involved in the overlap.

Commutator relations

$$[t, x]=u$$

between hermitian and antihermitian operators t, x, u are equivalent to a matrix representation [4]

$$\sum_{\chi}\sum_{\chi'} t_{\mu\chi} S^{-1}_{\chi\chi'} x_{\chi'\nu}-x_{\mu\chi} S^{-1}_{\chi\chi'} t_{\chi'\nu}=u_{\mu\nu} \tag{2.1}$$

if the expansion is carried out in a complete basis set $\{\chi\}$. This is equivalent to

$$\begin{aligned} x_{\mu\nu}=\frac{Q_{\mu\nu}}{Q^2_{\mu\nu}}\Big[&\sum_{\mu'}^{A} F_{\mu'\nu} x_{\mu\mu'}-\sum_{\nu'}^{B} F_{\nu'\mu} x_{\nu'\nu}+\sum_{\nu'\neq\nu}^{B} F_{\nu\nu'} x_{\mu\nu} \\ &-\sum_{\mu'\neq\mu}^{A} F_{\mu'\mu} x_{\mu'\nu}+u_{\mu\nu}\Big] \end{aligned} \tag{2.2}$$

with

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

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

If μ, μ' and ν, ν' are atomic orbitals on two different centers, (2.2) allows us to expand two-center terms $x_{\mu\nu}$ iteratively in single-center terms $x_{\mu\mu'}$ and $x_{\nu\nu'}$. Truncations in the expansion usually lead to approximate relations between the matrix elements of x, t and u. However, we have previously proved [1] that for $x=1$, $t=\underline{r}$, $u=0$ and $x=\underline{r}$, $t=\underline{r}$, $u=0$ the relations are accurate on any level of truncation. This means that charge and one component of the dipole moment can be conserved in finite basis set expansions. To guarantee invariance of the charges under rotation of the coordinate system, the calculations should be carried out in polyatomics in local coordinate systems and the moment along the internuclear axis is the one to be conserved. We suggested further that all AO's of an SCF calculation should be used as expansion functions χ in (2.1) for a subsequent population analysis. If $t=\underline{r}$ and x is a component of a multipole tensor, (2.2) is an approximation in a finite basis set. The errors resulting from truncations were calculated for quadrupole moment components z^2 and octupole moments components z^3 for a number of diatomics in their various basis sets in the following section. The explicit consequences of the operator formalism are given in an appendix.

3. Results and Discussion

In Table 1 we have listed the net charge, dipole, quadrupole and octupole moment components (with origin on atom A) along the internuclear axis in LiH, BH, FH, CO and LiF for Mulliken's, Löwdin's and our definition of atomic charges. The various basis sets in FH and LiF are listed according to increasing dipole moments. Besides the optimal minimal basis sets considered previously [1], double zeta subsets were taken from the work of Nesbet [5], Clementi [6, 7] and Cade and Huo [8]. Modifications of the basis set on H in FH were taken from McLean and Yoshimine [9] as well as polarization terms on H from [5, 6, 8]. Finally close to Hartree-Fock extended basis sets of McLean and Yoshimine [10] were considered. A comparison with experimental data on dipole moments was given previously [1]. Because of lack of information we are unable to provide a systematic comparison for quadrupole moments.

The results listed under Mulliken's definition are based on the assumption that any two-center moment integral is divided in two equal parts and distributed among the two atoms involved. This procedure conserves all moments. Thus the numbers in the Mulliken rows represent the exact moments of the underlying SCF wavefunctions. This does not mean, however, that there is consistency between the atomic charges and the higher moments obtained by equal partitioning. Unfortunately, the Mulliken analysis does not provide us with a direct clue for consistency. Only the consideration of charge transfer versus atomic polarization in the next paragraph yields some insight. At this point a comparison with Löwdin's

Table 1. Charge distributions and their higher moments (a.u.) with their respective errors

Molecule A B	Basis Set	Net Charge Q	Dipole moment z_A	Quadrupole moment z_A^2	Octupole moment z_A^3	Method
Li^+H^-	minimal	0.347	−2.318	−8.846	−36.365	Mulliken
		0.618	−2.318	−9.758 (10.3%)	−37.265 (2.5%)	Löwdin
		0.459	−2.318	−9.006 (1.8%)	−36.407 (0.1%)	Jug
B^+H^-	minimal	0.019	0.630	−6.912	−2.888	
		0.304	0.630	−7.751 (12.1%)	−5.297 (83.4%)	
		0.153	0.630	−7.169 (3.7%)	−3.947 (36.7%)	
F^-H^+	minimal	0.234	0.575	−2.224	−0.429	
		0.060	0.575	−2.826 (27.1%)	−2.048 (377%)	
		0.196	0.575	−2.410 (8.3%)	−1.157 (170%)	
	A	0.231	0.626	−2.476	−0.191	
		−0.004	0.626	−3.488 (40.8%)	−3.223 (1587%)	
		−0.050	0.626	−2.664 (7.6%)	−0.822 (330%)	
	B	0.442	0.758	−2.458	−0.367	
		0.166	0.758	−3.176 (29.2%)	−2.474 (574%)	
		0.344	0.758	−2.636 (7.2%)	−1.059 (189%)	
	C	0.529	0.761	−2.367	1.486	
		0.361	0.761	−2.793 (17.8%)	0.448 (69.9%)	
		0.426	0.761	−2.370 (0.1%)	1.479 (0.5%)	
	D	0.414	0.858	−2.275	1.736	
		0.237	0.858	−2.813 (23.6%)	0.440 (74.7%)	
		0.252	0.858	−2.395 (5.3%)	2.090 (20.4%)	
	E	0.347	0.910	−2.404	1.796	
		0.191	0.910	−2.992 (24.5%)	0.388 (78.3%)	
		0.177	0.910	−2.481 (3.2%)	1.637 (8.9%)	
	F	0.496	0.916	−2.317	1.370	
		0.290	0.916	−2.755 (18.9%)	0.291 (78.8%)	
		0.424	0.916	−2.455 (6.0%)	0.983 (28.2%)	
	G	0.484	0.925	−2.317	1.475	
		0.289	0.925	−2.618 (13.0%)	1.083 (26.6%)	
		0.417	0.925	−2.454 (5.9%)	1.081 (26.7%)	
	H	0.510	0.929	−2.296	1.460	
		0.305	0.929	−2.728 (18.8%)	0.394 (73.0%)	
		0.435	0.929	−2.429 (5.8%)	1.079 (26.1%)	
	I	0.501	0.971	−2.449	1.713	
		0.334	0.971	−2.782 (13.6%)	1.034 (39.6%)	
		0.449	0.971	−2.587 (5.6%)	1.424 (16.9%)	
C^+O^-	minimal	0.220	0.0375	−8.602	−23.619	
		0.245	0.0375	−10.577 (23.0%)	−29.444 (24.7%)	
		0.284	0.0375	−9.306 (8.1%)	−25.603 (8.4%)	
Li^+F^-	minimal	0.262	−1.376	−8.107	−35.984	
		0.340	−1.376	−9.905 (22.1%)	−40.884 (13.6%)	
		0.257	−1.376	−8.762 (8.1%)	−38.534 (7.1%)	

Molecule A B	Basis Set	Net Charge Q	Dipole moment z_A	Quadrupole moment z_A^2	Octupole moment z_A^3	Method
Li^+F^-	J	0.569	−2.357	−10.643	−51.346	Mulliken
		0.761	−2.357	−11.571 (8.7%)	−53.896 (5.0%)	Löwdin
		1.267	−2.357	−10.162 (4.4%)	−47.100 (8.2%)	Jug
	K	0.715	−2.375	−11.213	−52.690	
		0.801	−2.375	−11.983 (6.9%)	−54.696 (3.8%)	
		0.779	−2.375	−11.446 (2.1%)	−52.993 (0.6%)	

A Nesbet [5]; polar; set *B* plus $2p\sigma$, $2p\pi$ on *H*
B Nesbet [5]; double zeta; F: $1s$, $1s$, $2s$, $2s$, $2p\sigma$, $2p\sigma$, $2p\pi$, $2p\pi$
H: $1s$, $2s$
C McLean, Yoshimine [10]; extended; from [8] plus $3p\sigma$, $3d\sigma$, $3p\pi$ on H and $4d\pi$ on F
D Cade [8]; polar; set *H* plus $2p\sigma$, $2p\pi$ on H
E Clementi [6]; polar; set *I* plus $2p\sigma$, $2p\pi$ on H
F Clementi [7]; standard double zeta; $1s$, $2s$ on H from set *H*
G Cade [8]; double zeta; $1s$, $2s$ on H from [9]
H Cade [8]; double zeta; F: $1s$, $1s$, $2s$ $2s$, $2p\sigma$, $2p\sigma$, $2p\pi$, $2p\pi$
H: $1s$, $2s$
I Clementi [6]; double zeta; F: $1s$, $1s$, $2s$, $2s$, $2p\sigma$, $2p\sigma$, $2p\pi$, $2p\pi$
H: $1s$, $1s$
J McLean, Yoshimine [10]; extended; from [7] plus $2p$, $3d$, $4f$ on H and $3d$, $4f$ on F
K Clementi [7]; standard double zeta; $2p\sigma$, $2p\pi$ on Li with $2s$ exponents

definition is more conclusive. The results show that Löwdin's definition consistently gives larger errors in the higher moments than our definition. From the errors in the higher moments of our method we further conclude that only three cases yield reliable net charges: minimal basis set of LiH (0.46), McLean-Yoshimine's set of FH (0.43) and Clementi's double-zeta set of LiF (0.78). This conclusion is consistent with the fact that the experimental dipole moments for LiH (−2.31 a.u.), FH (0.715 a.u.) and LiF (−2.60 a.u.) are well reproduced by the above wavefunctions. From the above experimental and theoretical data, we would extrapolate the following polarities: 0.40 for FH, 0.46 for LiH and 0.85 for LiF. The table also shows that Nesbet's subsets are less balanced than Clementi's or Cade's. Although the dipole moments of Nesbet's sets are close to the experimental value, the errors in the higher moments reveal that the calculated net charges may not be reliable. That the basis set balance in the LCAO approach is of great importance is revealed also by the fact that introduction of 2p orbitals on hydrogen might not change the dipole moment of the wavefunction considerably, but has a significant effect on the charges. In the case of LiF we find the surprising result that the extended basis set of McLean and Yoshimine does not yield an improvement over Clementi's double-zeta set but tends to introduce an unbalance[1].

This seems to be supported by the overlap partitioning in Table 2 where the

---

[1] The problem lies in the π system and is possibly due to the fact that the authors use one $2p$-orbital on Li and two $2p$-orbitals on F, thus creating an undue emphasis on charge transfer to F.

Table 2. Overlap partitioning

Molecule			Overlap			
A B	Basis set	S_{AA}	S^{A}_{AB}	S^{B}_{AB}	S_{BB}	
$Li^{+}H^{-}$	minimal	2.288	0.365	0.365	0.981	Mulliken
		2.288	0.094	0.636	0.981	Löwdin
		2.288	0.254	0.476	0.981	Jug
$B^{+}H^{-}$	minimal	4.648	0.332	0.332	0.686	
		4.648	0.049	0.615	0.686	
		4.648	0.199	0.465	0.686	
$F^{-}H^{+}$	minimal	9.043	0.191	0.191	0.573	
		9.043	0.018	0.364	0.573	
		9.043	0.153	0.229	0.573	
	A	8.928	0.314	0.314	0.453	
		8.928	0.079	0.549	0.453	
		8.928	0.032	0.595	0.453	
	B	9.302	0.151	0.151	0.406	
		9.302	−0.124	0.425	0.406	
		9.302	0.055	0.246	0.406	
	C	9.235	0.295	0.295	0.175	
		9.235	0.127	0.464	0.175	
		9.235	0.191	0.398	0.175	
	D	9.127	0.300	0.300	0.284	
		9.127	0.122	0.477	0.284	
		9.127	0.141	0.458	0.284	
	E	9.005	0.350	0.350	0.300	
		9.005	0.194	0.507	0.300	
		9.005	0.183	0.518	0.300	
	F	9.289	0.218	0.218	0.285	
		9.289	0.014	0.422	0.285	
		9.289	0.148	0.288	0.285	
	G	9.276	0.220	0.220	0.294	
		9.276	0.026	0.413	0.294	
		9.276	0.154	0.285	0.294	
	H	9.318	0.205	0.205	0.284	
		9.318	0.001	0.409	0.284	
		9.318	0.131	0.278	0.284	
	I	9.247	0.262	0.262	0.235	
		9.247	0.095	0.430	0.235	
		9.247	0.213	0.312	0.235	
$C^{+}O^{-}$	minimal	5.253	0.527	0.527	7.692	
		5.253	0.501	0.553	7.692	
		5.253	0.462	0.591	7.692	
$Li^{+}F^{-}$	minimal	2.505	0.233	0.233	9.029	
		2.505	0.155	0.311	9.029	
		2.505	0.235	0.231	9.029	

Table 2 (continued)

Molecule		Overlap				
A B	Basis set	S_{AA}	S_{AB}^{A}	S_{AB}^{B}	S_{BB}	
Li^+F^-	*J*	2.137	0.292	0.292	9.277	Mulliken
		2.137	0.101	0.484	9.277	Löwdin
		2.137	−0.405	0.990	9.277	Jug
	K	2.136	0.151	0.151	9.577	
		2.136	0.065	0.237	9.577	
		2.136	0.080	0.222	9.577	

Basis sets *A*–*K* as in Table 1

Table 3. Hybrid and Charge Partitioning of Dipole Moment

		Dipole Moment				
Molecule	Basis set	Hybrid		Charge	Total	
A B		D_A	D_B	D_Q	D	
LiH	minimal	−1.415	0.141	−1.044	−2.318	Mulliken
		−0.457	0.000	−1.861	−2.318	Löwdin
		−0.938	0.000	−1.380	−2.318	Jug
BH	minimal	0.615	0.057	−0.042	0.630	
		1.332	0.000	−0.702	0.630	
		0.981	0.000	−0.351	0.630	
FH	minimal	0.151	0.016	0.408	0.575	
		0.466	0.000	0.109	0.575	
		0.232	0.000	0.343	0.575	
	A	0.084	0.139	0.403	0.625	
		0.559	0.071	−0.004	0.625	
		0.357	0.354	−0.086	0.625	
	B	0.097	−0.107	0.768	0.758	
		0.466	0.000	0.292	0.758	
		0.155	0.000	0.602	0.758	
	C	−0.279	0.121	0.918	0.761	
		0.123	0.012	0.626	0.761	
		−0.083	0.106	0.738	0.761	
	D	0.011	0.125	0.721	0.858	
		0.424	0.020	0.413	0.858	
		0.279	0.132	0.446	0.858	
	E	0.084	0.222	0.604	0.910	
		0.523	0.053	0.334	0.910	
		0.367	0.228	0.314	0.910	
	F	0.044	0.012	0.861	0.916	
		0.409	0.000	0.507	0.916	
		0.177	0.000	0.739	0.916	
	G	0.060	0.022	0.842	0.924	
		0.418	0.000	0.506	0.924	
		0.196	0.000	0.729	0.924	

Table 3 (continued)

Molecule	Basis set	Dipole Moment				
		Hybrid		Charge	Total	
A B		D_A	D_B	D_Q	D	
FH	*H*	0.042	0.000	0.886	0.929	Mulliken
		0.396	0.000	0.532	0.929	Löwdin
		0.170	0.000	0.759	0.929	Jug
	I	0.019	0.082	0.870	0.971	
		0.391	0.000	0.580	0.971	
		0.187	0.000	0.784	0.971	
CO	minimal	0.604	−0.099	−0.467	0.038	
		1.193	−0.633	−0.522	0.038	
		0.955	−0.312	−0.605	0.038	
LiF	minimal	−0.601	−0.027	−0.747	−1.376	
		−0.157	−0.249	−0.970	−1.376	
		−0.534	−0.099	−0.742	−1.376	
	J	−0.837	0.103	−1.623	−2.357	
		−0.147	−0.041	−2.169	−2.357	
		0.825	0.429	−3.612	−2.357	
	K	−0.318	0.018	−2.074	−2.375	
		0.019	−0.075	−2.319	−2.375	
		−0.073	−0.027	−2.275	−2.375	

Basis sets *A* – *K* as in Table 1.

Table 4. Partitioning of the charge distribution of the lowest-lying MO's in atomic parts

Molecule	Basis set		Electronic charge on atom		Method
AB		MO	A	B	
LiH	minimal	1σ	1.99860	0.00140	Mulliken
			1.99944	0.00056	Löwdin
			1.99986	0.00014	Jug
BH	minimal	1σ	2.00078	−0.00078	
			2.00013	−0.00013	
			1.99995	0.00005	
FH	minimal	1σ	2.00041	−0.00041	
			2.00005	−0.00005	
			1.99994	0.00006	
	A	1σ	1.99686	0.00314	
			1.99979	0.00021	
			1.99948	0.00052	
	B	1σ	1.99942	0.00058	
			1.99988	0.00002	
			1.99994	0.00006	

Molecule	Basis set		Electronic charge on atom		Method
AB		MO	A	B	
FH	*C*	1σ	1.99947	0.00053	Mulliken
			1.99996	0.00004	Löwdin
			2.00006	−0.00006	Jug
	D	1σ	2.00006	−0.00006	
			2.00000	−0.00000	
			2.00001	−0.00001	
	E	1σ	1.99880	0.00120	
			1.99995	0.00005	
			2.00000	−0.00000	
	F	1σ	1.99946	0.00054	
			1.99998	0.00002	
			1.99994	0.00006	
	G	1σ	2.00007	−0.00007	
			2.00000	−0.00000	
			2.00000	−0.00000	
	H	1σ	2.00006	−0.00006	
			2.00000	−0.00000	
			2.00000	−0.00000	
	I	1σ	1.99925	0.00075	
			1.99999	0.00001	
			1.99996	0.00004	
CO	minimal	1σ	−0.00156	2.00156	
			−0.00014	2.00014	
			0.00026	1.99974	
		2σ	2.00077	−0.00077	
			2.00023	−0.00023	
			1.99997	0.00003	
LiF	minimal	1σ	−0.00053	2.00053	
			0.00001	1.99999	
			−0.00008	2.00008	
	J	1σ	−0.00002	2.00002	
			−0.00000	2.00000	
			−0.00000	2.00000	
	K	1σ	0.00047	1.99953	
			0.00002	1.99998	
			−0.00010	2.00010	

Basis sets *A* – *K* as in Table 1

McLean-Yoshimine case tends to overpolarization, a fact which is rare but cannot be ruled out in a finite basis set expansion [4]. Löwdin's definition yields another such case for Nesbet's subset. Table 2 further reveals that the ratio of atomic to overlap charges varies considerably in the different basis set: 0.30 – 0.70 in FH, 0.30–0.58 in LiF.

Table 3 is helpful in assessing the validity of the Mulliken approximation. All cases in which only *s* functions on hydrogen are used should yield zero hybrid moment on this atom. The error in the Mulliken approximation is often small, but it is significant in LiH. The differences in the other hybrid moments are mostly quantitative with the exception of Clementi's set on LiF. Mulliken's analysis, i.e. equal partitioning of all moments involving overlap between two atoms, predicts that the F atom is slightly polarized towards Li which in turn is highly polarized towards F. We assess that both atoms have little polarization with Li polarized towards F and F polarized away from Li. Both Mulliken and our definition are out of place for the McLean-Yoshimine set, whereas Löwdin's definition parallels ours for the Clementi set, thus accidentally supporting the latter.

To complete the picture we have analyzed the 1σ orbital partitioning between the two atoms of the diatomics. We find that our definition reduces the overpolarization by an order of magnitude compared to Mulliken's analysis, but cannot avoid it altogether. It shows, however, the right trend, i.e. we can reduce the overpolarization below a desirable threshold by expanding the basis set for the population analysis. It would be interesting to see whether exponent reoptimization of the inner shell orbitals could reduce the error further.

4. Conclusion

We find that the commutator expansion method developed by us for population analyses in molecules looks very promising and should be pursued further. Evidence from multipole moment and hybrid moment analysis as well as 1σ MO investigations emphasizes the advantage over Mulliken's or Löwdin's definition. We summarize our results as follows:

1. A population analysis is linked to the underlying SCF wavefunction. The commutator expansions can reproduce more or less closely only what the wavefunction implies.
2. A statement about atomic charges can be meaningful only if the expectation values of relevant quantities are close to experimental values. In this respect, the energy is not a relevant quantity.
3. New criteria for charge distributions have to be developed. Looking for consistency between charge distributions and their higher moments seems to be the right direction.

In this paper we could not include discussions of various other methods [11–13] since the question of basis set dependence of charge and multipole moments was not comprehensively raised by these authors.

Acknowledgement. The calculations were carried out with MOLPRO and INTE (QCPE 158), at the University of Stuttgart, Indiana University, St. Louis University and the University of Missouri at St. Louis. We thank R. Counts, W. Meyer and J. Chickos for computer related assistance at various stages of this project.

Appendix

Let us call atoms M, N, atomic orbitals μ, ν, atomic core charges Z_M, total gross population on atoms n_M and total gross populations in AO's n_μ. The population analysis can be presented as a sequence of equalities for net charge Q in terms of overlap S and density matrix P:

$$\begin{aligned}
Q&=\sum_{M} Z_M-\sum_{M}\sum_{N}\sum_{\mu}^{M}\sum_{\nu}^{N} P_{\mu\nu}S_{\mu\nu}\\
&=\sum_{M}\left(Z_M-\sum_{\mu}^{M}\left(\sum_{\mu'}^{M} P_{\mu\mu'}S_{\mu\mu'}+\sum_{N\neq M}\sum_{\nu}^{N} P_{\mu\nu}S_{\mu\nu}\right)\right)\\
&=\sum_{M}\left(Z_M-\sum_{\mu}^{M}\left(\sum_{\mu'}^{M} P_{\mu\mu'}S_{\mu\mu'}+\sum_{N\neq M}\sum_{\nu}^{N} P_{\mu\nu}S^{(\mu)}_{\mu\nu}\right)\right)\\
&=\sum_{M}\left(Z_M-\sum_{\mu}^{M} n_\mu\right)\\
&=\sum_{M}(Z_M-n_M)\\
&=\sum_{M} Q_M
\end{aligned}\tag{A.1}$$

Relevant for our procedure is step 3 which is based on $S_{\mu\nu}=\frac{1}{2}\,(S^{(\mu)}_{\mu\nu}+S^{(\nu)}_{\mu\nu})$ where $S^{(\mu)}_{\mu\nu}$ is determined by (2.2) with $x=1$ and $t=z$.

The partitioning of dipole moments D for neutral molecules is analogous except for the occurrence of hybrid moments. Atomic hybrid moments originate from non-vanishing contributions of the dipole operator for which the overlap integrals vanish [14]. We call $D^{(Q)}$ the charge part and $D^{(H)}$ the hybrid part of the dipole moment. z is a coordinate along the internuclear axis.

$$\begin{aligned}
D_z&=\sum_{M} Z_M z_M-\sum_{M}\sum_{N}\sum_{\mu}^{M}\sum_{\nu}^{N} P_{\mu\nu}z_{\mu\nu}\\
&=\sum_{M}\left(Z_M z_M-\sum_{\mu}^{M}\left(\sum_{\mu'}^{M} P_{\mu\mu'}z_{\mu\mu'}+\sum_{N\neq M}\sum_{\nu}^{N} P_{\mu\nu}z_{\mu\nu}\right.\right.\\
&\qquad\left.\left.+\sum_{\mu''\neq\mu'}^{M} P_{\mu\mu''}z_{\mu\mu''}+\sum_{N\neq M}\sum_{\nu'\neq\nu}^{N} P_{\mu\nu}z_{\mu\nu'}\right)\right)\\
&=\sum_{M}\left(Z_M z_M-\sum_{\mu}^{M}\left(\sum_{\mu'}^{M} P_{\mu\mu'}z_{\mu\mu'}+\sum_{N\neq M}\sum_{\nu}^{N} P_{\mu\nu}z^{(\mu)}_{\mu\nu}\right)\right)\\
&\qquad+\sum_{\mu''\neq\mu'} P_{\mu\mu''}z_{\mu\mu''}\quad+\sum_{N\neq M}\sum_{\nu'\neq\nu}^{N} P_{\mu\nu}z^{(\mu)}_{\mu\nu'}\Bigg)\Bigg)\\
&=\sum_{M}\left(Z_M z_M-\sum_{\mu}^{M} n_\mu z_M+\sum_{\mu}^{M} D^{(H)}_{z\mu}\right)\\
&=\sum_{M}(Q_M z_M+D^{(H)}_{zM})\\
&=\sum_{M}(D^{(Q)}_{zM}+D^{(H)}_{zM})
\end{aligned}\tag{A.2}$$

Here $S_{\mu\mu''}=S_{\mu\nu'}=0$ for all μ'', ν'. Step 3 is the relevant step where

$$x_{\mu\nu}=\tfrac{1}{2}(x^{(\mu)}_{\mu\nu}+x^{(\nu)}_{\mu\nu})\tag{A.3}$$

according to (2.2) with $x=z$ and $t=z$. For quadrupole moment operator $x=z^2$ and octupole moment operator $x=z^3$, (A.3) holds only approximately. This leads to the errors tabulated in Table 1.

References

1. Jug,K.: Theoret. Chim. Acta (Berl.) **31**, 63 (1973)
2. Mulliken,R.S.: J. Chem. Phys. **23**, 1833 (1955)
3. Löwdin,P.O.: J. Chem. Phys. **21**, 374 (1953)
4. Jug,K.: Theoret. Chim. Acta (Berl.) **29**, 9 (1973)
5. Nesbet,R.K.: J. Chem. Phys. **36**, 1518 (1962)
6. Clementi,E: J. Chem. Phys. **36**, 33 (1962)
7. Clementi,E: J. Chem. Phys. **40**, 1944 (1964)
8. Cade,P.E., Huo,W.M.: J. Chem. Phys. **47**, 614 (1967)
9. McLean,A.D., Yoshimine,M.: Suppl. IBM J. Res. Dev., 169 (1967)
10. McLean,A.D., Yoshimine,M.: Suppl. IBM J. Res. Dev., 1, 2 (1967)
11. Politzer,P., Harris,R.R.: J. Am. Chem. Soc. **92**, 6451 (1970)
12. Politzer,P., Politzer,A.: J. Am. Chem. Soc. **95**, 5450 (1973)
13. Fliszar,S., Kean,G., Macaulay,R.: J. Am. Chem. Soc. **96**, 4353 (1974); Fliszar,S., Goursot,A., Dugas,H.: J. Am. Chem. Soc. **96**, 4358 (1974)
14. Pople,J.A., Beveridge,D.L.: Approximate molecular orbital theory, p. 87. New-York: McGraw-Hill 1970

Prof. Dr. K. Jug
Institut für Physikalische Chemie und
Elektrochemie der
Technischen Universität Hannover
D-3000 Hannover
Callinstraße 46, Eingang I
Federal Republic of Germany