Effects of Polarization on Charge Distributions and Integral Approximations

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Polarization factors derived in a previous paper [1] are presented for $1s$, $2s$, $2p\sigma$ and $2p\pi$ orbitals on two centers. The formulas for gross atomic populations and integral approximations are tested in diatomics. It is found that our definition of atomic charges proposed earlier is far superior to the Mulliken approximation. With proper partitioning into charge and hybrid parts the total dipole moment of the wavefunction can be obtained with great accuracy. The application of the formulas to two-center hybrid repulsion integrals is less satisfactory in the lowest-order approximation.

Die Polarisationsfaktoren einer früheren Arbeit [1] werden für $1s$-, $2s$-, $2p\sigma$- und $2p\pi$-Orbitale an zwei Zentren angegeben. Die Formeln für Atomladungsverteilungen und Integralapproximationen werden in zweiatomigen Molekülen geprüft. Man findet, daß unsere vorgeschlagene Definition von Atomladungen der Mulliken-Näherung weit überlegen ist. Bei geeigneter Aufteilung in Ladungs- und Hybridanteil kann das Dipolmoment der Wellenfunktion mit großer Genauigkeit erhalten werden. Die Anwendung der Formeln auf Zwei-Zentren-Hybridintegrale der Elektronenwechselwirkung ist weniger zufriedenstellend in der niedrigsten Approximationsstufe.

1. Introduction

Recently, we developed the basis for an approximate molecular orbital method whose chief characteristic is the lack of empirical adjustment [1, 2]. The basic idea was to use commutator equations $u = [t, x]$ between hermitian and antihermitian operators to establish approximate integral relations on the basis of truncated expansions for integrals over atomic orbitals μ, v on different centers. We have tested the accuracy of approximations for β integrals over a core Hamiltonian in the case of two equal $2s$, $2p\sigma$ and $2p\pi$ orbitals on different centers [2]. In this paper, we test the accuracy of charge distributions and certain selected repulsion integrals in heteropolar diatomics. After a brief formulation of the method, we present the polarization factors for $1s$, $2s$, $2p$ orbitals. We then discuss the dipole moments of various diatomics and show that a satisfactory definition of atomic charge distributions in molecules can be gained on the basis of our considerations. The use of this definition of atomic charge distributions in polyatomics is straightforward. Our results for repulsion integrals show that the lowest order expansions are sometimes insufficient to guarantee the same accuracy as in one-electron integrals.

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2. The General Method

A commutator equation

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

with hermitian and antihermitian operators u, t, x is equivalent to a matrix representation in a complete orthogonal or non-orthogonal basis set. For the case of one-electron operators the following expansion over non-orthogonal orbitals χ, χ' seems to be most convenient

with

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

$$u_{\mu\nu} = \langle \mu | u | \nu \rangle \quad \text{etc.} \tag{2.2}$$

if μ and ν are atomic orbitals on different centers. S^{-1} is the inverse of the overlap matrix. We denote the adjugate matrix by $\tilde{S}$. By definition of S^{-1}

$$\tilde{S} = S^{-1} \det S \tag{2.3}$$

holds. With (2.2) and (2.3) an element $x_{\mu\nu}$ can be expressed exactly in the following way

$$
\begin{aligned}
x_{\mu\nu} = &\left(\sum_{\chi} t_{\mu\chi}\tilde{S}_{\chi\mu} - t_{\chi\nu}\tilde{S}_{\chi\nu} \right)^{-1} \\
&\times \left[\frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\mu} - t_{\mu\chi}\tilde{S}_{\chi\nu})(x_{\mu\mu} + x_{\nu\nu}) \right. \\
&+ \frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\mu} + t_{\mu\chi}\tilde{S}_{\chi\nu})(x_{\mu\mu} - x_{\nu\nu}) \\
&+ \sum_{\substack{\mu' \neq \mu \\ \nu' \neq \nu}} \left\{ \frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\mu'} - t_{\mu\chi}\tilde{S}_{\chi\nu'})(x_{\mu\mu'} + x_{\nu'\nu}) \right. \\
&+ \frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\mu'} + t_{\mu\chi}\tilde{S}_{\chi\nu'})(x_{\mu\mu'} - x_{\nu'\nu}) \\
&+ \frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\nu'} - t_{\mu\chi}\tilde{S}_{\chi\mu'})(x_{\mu\nu'} + x_{\mu'\nu}) \\
&+ \left. \frac{1}{2}\sum_{\chi}(t_{\chi\nu}\tilde{S}_{\chi\nu'} + t_{\mu\chi}\tilde{S}_{\chi\mu'})(x_{\mu\nu'} - x_{\mu'\nu}) \right\} \\
&+ \left. u_{\mu\nu} \det S \right].
\end{aligned}
\tag{2.4}
$$

The right side of (2.4) consists of seven terms: the Mulliken approximation for x and its polarization, the other single-center contributions and their polarization, the rest of the two-center contributions and their polarization and the contribution of u. Our previous work [1, 2] was concerned with the first two terms and the dominant contribution of the third and fourth term in cases where μ and ν are *not equivalent* orbitals on different centers. We have neglected contributions from terms five and six and kept seven where it was different from

zero. The following commutator equations seem to be of interest for the property listed on the right

$$[r, 1] = 0 \qquad \text{overlap} \qquad (2.5a)$$

$$[r, r] = 0 \qquad \text{dipole moment} \qquad (2.5b)$$

$$[r, V] = 0 \qquad \text{potential energy} \qquad (2.5c)$$

$$[r, T] = p \qquad \text{kinetic energy} \qquad (2.5d)$$

$$[r, h] = p \qquad \text{core energy} \qquad (2.5e)$$

$$[r, p] = -1 \qquad \text{slope of overlap} \qquad (2.5f)$$

$$\left[r_1 + r_2, \frac{1}{r_{12}} \right] = 0 \qquad \text{electronic interaction energy.} \qquad (2.5g)$$

The last equation fits into a two-electron form of (2.4). In all relations $t = r$. For this particular case, the formalism conserves the dipole moment on any level of truncation of (2.4). This is due to the symmetry $x = t$ of (2.5b) as an inspection of (2.2) shows. We derive now an approximate formula for $x_{\mu\nu}$ with four expansion functions, μ, μ' on atom A and ν, ν' on atom B, in the case $t = r$. For the sake of simplicity and practicability we drop all terms containing products of two or more overlap integrals in the polarization factors x. Applications in Section 4 show that this means an insignificant loss of accuracy in the dipole moment.

$$x_{\mu\nu} = \tfrac{1}{2} S_{\mu\nu}(1 + x_{\mu\nu}) x_{\mu\mu} + \tfrac{1}{2} S_{\mu\nu}(1 - x_{\mu\nu}) x_{\nu\nu}$$
$$+ \tfrac{1}{2} S_{\mu'\nu}(1 + x_{\mu'\nu}) x_{\mu\mu'} + \tfrac{1}{2} S_{\mu\nu'}(1 - x_{\mu\nu'}) x_{\nu'\nu}$$
$$+ u_{\mu\nu} \det S$$

with $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.6)$

$$x_{\mu\nu} = \frac{2 z_{\mu\nu} - S_{\mu\nu}(z_{\mu\mu} + z_{\nu\nu}) - S_{\mu'\nu} z_{\mu\mu'} - S_{\mu\nu'} z_{\nu\nu'}}{S_{\mu\nu}(z_{\mu\mu} - z_{\nu\nu})}$$

$$\det S = \begin{cases} (1 - S_{\mu\nu}^2)(1 - S_{\mu'\nu'}^2) \\ (1 - S_{\mu'\nu}^2)(1 - S_{\mu\nu'}^2) \end{cases} \quad \text{for} \quad \begin{Bmatrix} \mu, \nu \\ \mu', \nu' \end{Bmatrix} \quad \text{of same type}$$

z is a component of r in a local coordinate system, in particular along the internuclear axis. $x_{\mu'\nu}$ and $x_{\mu\nu'}$ are defined similarly to $x_{\mu\nu}$. Inspection of $x_{\mu\nu}$ shows that hybrid parts are eliminated from the two-center dipole moment. The rest contributes to the charge redistribution. The corresponding hybrid parts to those of $x_{\mu\nu}$ are explicitly presented in terms three and four of (2.6). In the following, we calculate polarization factors x for various ratios of exponents of $1s$, $2s$, $2p$ orbitals on two centers.

Then we apply formula (2.6) to overlap, dipole moment and electronic repulsion energy.

3. Polarization Factors

If $\mu\nu$ approaches formally an average of $\mu\mu$ and $\nu\nu$ in the united atom limit, then μ' and ν' are not essential. Otherwise the type of μ' and ν' is fixed by the condition that the united atom limit of $\mu\nu$ is represented by an average of $\mu\mu'$

Table 1. Polarization factors $\varkappa$ for $1s$, $2s$, $2p$ orbitals on two centers[a]

$$\varkappa_{11} = 1 - \frac{2\langle 2p\sigma_a(\zeta_a)|1s_b(\zeta_b)\rangle}{\varrho_a\langle 1s_a(\zeta_a)|1s_b(\zeta_b)\rangle}$$

$$\varkappa_{ss} = 1 - \frac{\sqrt{10}\langle 3p\sigma_a(\zeta_a)|2s_b(\zeta_b)\rangle}{\varrho_a\langle 2s_a(\zeta_a)|2s_b(\zeta_b)\rangle}$$

$$\varkappa_{\sigma\sigma} = 1 - \frac{\sqrt{8}\langle 3d\sigma_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle + \sqrt{10}\langle 3s_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle}{\varrho_a\langle 2p\sigma_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle}$$

$$\varkappa_{\pi\pi} = 1 - \frac{\sqrt{6}\langle 3d\pi_a(\zeta_a)|2p\pi_b(\zeta_b)\rangle}{\varrho_a\langle 2p\pi_a(\zeta_a)|2p\pi_b(\zeta_b)\rangle}$$

$$\varkappa_{1s} = 1 - \frac{2\langle 2p\sigma_a(\zeta_a)|2s_b(\zeta_b)\rangle}{\varrho_a\langle 1s_a(\zeta_a)|2s_b(\zeta_b)\rangle}$$

$$\varkappa_{1\sigma} = 1 - (2\langle 2p\sigma_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle - \langle 2p\sigma_a(\zeta_a)|2p\sigma_a(\zeta_a')\rangle \langle 2p\sigma_a(\zeta_a')|2p\sigma_b(\zeta_b)\rangle$$
$$- \frac{\zeta_a}{\zeta_b'}\langle 1s_a(\zeta_a)|1s_b(\zeta_b')\rangle \langle 2p\sigma_b(\zeta_b')|2p\sigma_b(\zeta_b)\rangle)/(\varrho_a\langle 1s_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle)$$

$$\varkappa_{s\sigma} = 1 - \sqrt{\frac{5}{2}}(2\langle 3p\sigma_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle - \langle 3p\sigma_a(\zeta_a)|2p\sigma_a(\zeta_a')\rangle \langle 2p\sigma_a(\zeta_a')|2p\sigma_b(\zeta_b)\rangle$$
$$- \frac{\zeta_a}{\zeta_b'}\langle 2s_a(\zeta_a)|2s_b(\zeta_b')\rangle \langle 3p\sigma_b(\zeta_b')|2p\sigma_b(\zeta_b)\rangle)/(\varrho_a\langle 2s_a(\zeta_a)|2p\sigma_b(\zeta_b)\rangle)$$

[a] Abbreviations: $11 = 1s_a 1s_b$, $ss = 2s_a 2s_b$ etc.

and vv' in a natural way. This suffices to guarantee a proper behaviour of the approximation (2.6) for small and large internuclear distances.

For practical purposes we have listed the polarization factors $\varkappa$ of Eq. (2.6) used for $1s$, $2s$, $2p\sigma$ and $2p\pi$ orbitals in Table 1. These are simple combinations of overlap integrals over Slater orbitals. Exponents ζ_a and ζ_b refer to the two orbitals on atom A and B for which the polarization factors are calculated; ζ_a' and ζ_b' refer to the complementary orbitals used in the expansion, e.g. $2p\sigma_a$ and $1s_b$ for $\varkappa_{1s_a 2p\sigma_b}$. We have calculated these seven polarization factors for various ratios $\zeta = \zeta_a/\zeta_b$ and internuclear distances $\varrho_a = \zeta_a R$. $\zeta_a' = \zeta_a/3.5$ and $\zeta_b' = 3.5\zeta_b$ was assumed for $\varkappa_{1\sigma}$ and $\zeta_a' = \zeta_a$, $\zeta_b' = \zeta_b$ for $\varkappa_{s\sigma}$. This represents the Slater orbitals for first-row atoms fairly well. In Section 4, we use the actual basis set orbitals for expansion.

The results are in Figs. 1–4. $\varkappa = 0$ means equal weighting factors for contributions to atoms A and B. $\varkappa = 1$ means the whole contribution goes to A, $\varkappa = -1$ the whole contribution goes to B. $\varkappa > 1$ and $\varkappa < -1$ characterizes cases with "overpolarization", i.e. where a simple partitioning in two positive parts cannot adequately describe the situation. In Fig. 1 the behaviour of $\varkappa$ for $1s$ and $2s$ orbitals can be simply characterized as follows: If the orbital on atom A is more contracted than the orbital on atom B ($\zeta < 1$) the contribution to atom A is increased. For a more diffuse orbital on A ($\zeta > 1$), it is decreased. With increasing internuclear distance the contribution to the atom with the more contracted orbital increases. The polarization factor approaches $+1$ or -1. A similar behaviour is shown in Fig. 2 for $2p\pi$ orbitals. The complicated
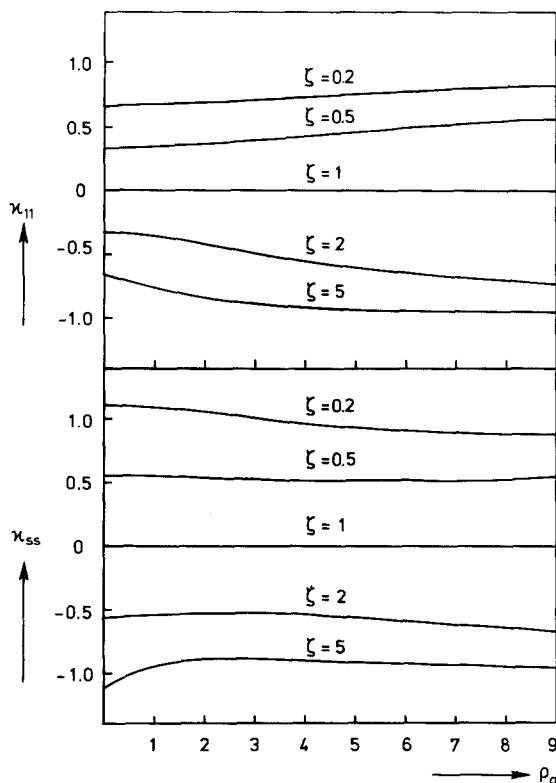
Fig. 1. Polarization factors $\varkappa$ for $1s_a 1s_b$ and $2s_a 2s_b$ charge distributions in dependence of $\varrho_a = \zeta_a R$; ζ_a orbital exponent of atom A, R internuclear distance (in atomic units), $\zeta = \zeta_b / \zeta_a$

dependence of $\varkappa$ for $2p\sigma$ orbitals can be explained in terms of the nodal property of the overlap integral. Here $\varkappa_{\sigma\sigma} S_{\sigma\sigma}$ is the relevant quantity which does not vanish when $S_{\sigma\sigma}$ does. The singularity of $\varkappa$ here means a shift of node of x_{ab} as compared to the Mulliken approximation. Fig. 3 shows the polarization of a $1s_a 2s_b$ distribution. Here $\varkappa$ is different from zero for $\zeta = 1$. This means in this case that for equal exponents more charge goes to the atom with the $1s$ orbital than to the atom with the $2s$ orbital. This is not surprising, since the center of charge is not in the middle between atoms A and B, but closer to A.

The curves for $\varkappa_{1\sigma}$ and $\varkappa_{s\sigma}$ show a different asymptotic behaviour for large internuclear distances from the previous ones. However for intermediate distances the interpretation is simpler. For orbitals of equal type more contribution goes to the center with the more contracted orbital, whereas here is an overall shift of weight to atom A similar to $\varkappa_{1s}$. The weights are not equal for $\zeta = 1$. There is a singularity for $R = 0$ in these two cases. This is due to the fact that we are dealing with the first two members of two different complete sets which are overcomplete in this limit. This problem could be avoided by using sets with flexible exponents which approach each other pairwise for $R = 0$. There is, however, no practical importance in the above failure.
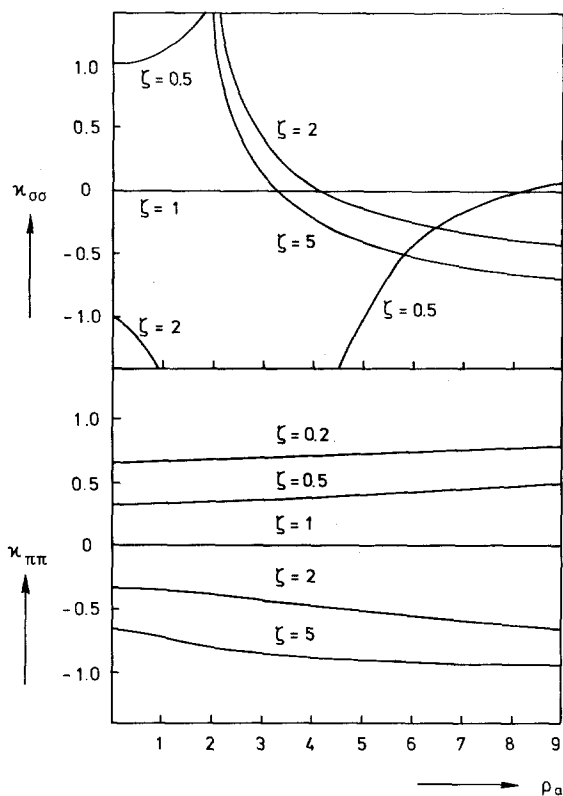
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Fig. 2. Polarization factors $\varkappa$ for $2p\sigma_a2p\sigma_b$ and $2p\pi_a2p\pi_b$ charge distributions in dependence of $\varrho_a = \zeta_a R$; ζ_a orbital exponent of atom A, R internuclear distance (in atomic units), $\zeta = \zeta_b/\zeta_a$

Fig. 3. Polarization factors $\varkappa$ for $1s_a2s_b$ charge distributions in dependence of $\varrho_a = \zeta_a R$; ζ_a orbital exponent of atom A, R internuclear distance (in atomic units), $\zeta = \zeta_b/\zeta_a$

Fig. 4. Polarization factors $\varkappa$ for $1s_a 2p\sigma_b$ and $2s_a 2p\sigma_b$ charge distributions in dependence of $\varrho_a = \zeta_a R$; ζ_a orbital exponent of atom A, R internuclear distance (in atomic units), $\zeta = \zeta_b/\zeta_a$
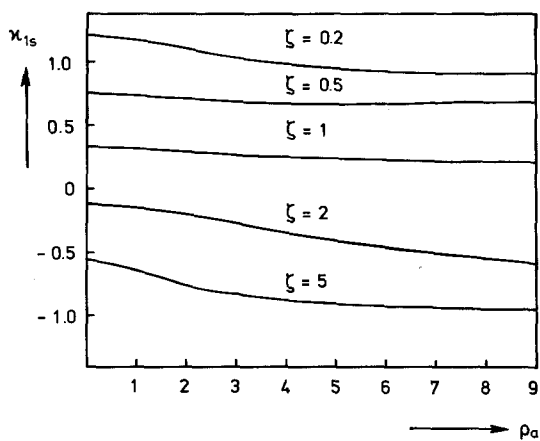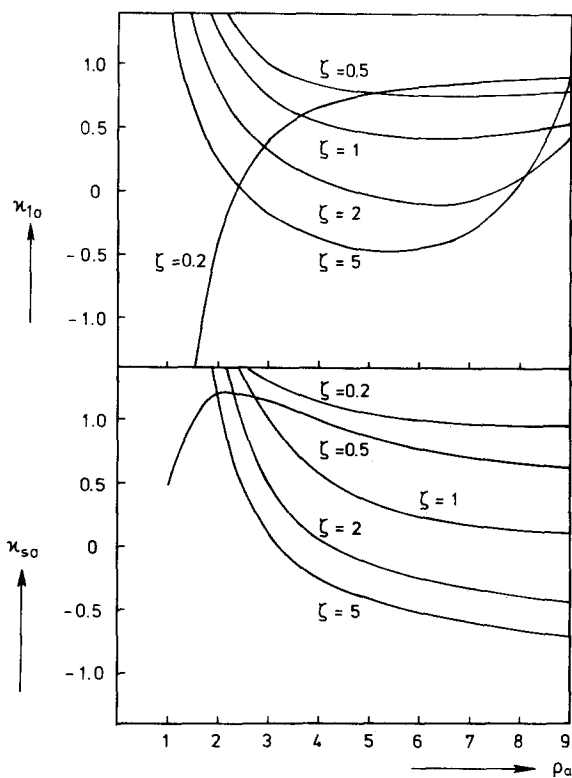
4. Charge Distributions and Dipole Moments

Among the concepts of molecular orbital theory, which are most popular among chemists is the assignment of a formal charge to an atom in a molecule. Such a definition avoids the complicated analysis of density contour maps and would offer us a simple tool in reactivity considerations. Unfortunately, the assignment of charge contributions to atoms in molecules is not unique, even if we use atomic basis sets centered at the different atoms. There exist overlap contributions $c_a c_b S_{ab}$ between two orbitals a, b on different centers A and B. Most popular is a procedure attributed to Mulliken [3], but also suggested by Daudel [4], to partition this contribution equally among the two atoms. Recently it became apparent, that the Mulliken analysis would lead unsatisfactory conclusions, e.g. about dipole moments. Three different alternatives have been proposed:

a) the use of different weighting factors for the partitioning among two atoms [5],

b) the use of Löwdin orthogonalized orbitals [6] each of which is completely attributed to a particular atom [7],

c) the definition of regions of space which are exclusively attributed to each of the atoms in a molecule [8].

Table 2. Net charges in heteronuclear diatomics

	Ransil wavefunction [12]			STO basis [13]	
	Mulliken	Christoffersen	This work	CNDO	INDO
Li^+H^-	0.35	0.51	0.62	0.27	0.29
B^+H^-	0.02	−0.12	0.30	0.08	0.08
F^-H^+	0.23	0.39	0.06	0.23	0.27
C^+O^-	0.17	0.55	0.19	0.08	0.07
Li^+F^-	0.28	0.48	0.37	0.56	0.58

Approach c) seems to be rather untractable and has been tested only in linear systems [9]. Approach b) is definitely open to critique because orthogonalization can be achieved only by contributions of other atoms to a nonorthogonal orbital. Thus the assignment of the resulting orthogonalized orbital to a particular atom is arbitrary. Cusachs and Politzer [10] have compared the Mulliken analysis and Löwdin analysis in diborane. The charge distributions of the same wavefunction were completely different. To avoid practical and methodical difficulties approach a) seems to offer the greatest possibilities. Our approach is in fact of this type. It differs from Christoffersen's in a sense that Christoffersen uses the coefficients of an SCF calculation to define weighting factors, whereas we obtain weighting factors from the nature of overlap distribution alone. It would be proper here to state, that our weighting factors come close to Löwdin's idea [11] to distribute the overlap among the atoms in such a way that the dipole moment of the distribution is conserved. In the simplest cases our procedure [1] yields indeed this result. However, in cases where overlap distributions of type $1s_a2p\sigma_b$ or $2s_a2p\sigma_b$ are involved our formulas are more general than Löwdin's because they take care of the hybrid dipole parts.

In Table 2 we have compared net charges for several selected diatomics LiH, BH, HF, CO and LiF in Mulliken's, Christoffersen's and our approximation based on Ransil's [12] optimized minimal basis sets as well as CNDO and INDO type calculations [13]. The differences in results could not be more striking. To determine which atomic distribution is most appropriate, we have calculated dipole moments with these charge distributions. These are listed under A in Table 3. The total dipole moment should properly be calculated as consisting of two parts: the charge part and the hybrid part [13]. The charge part is calculated with the weighted overlap integrals according to (2.6) with $x=1$. Only the first two terms contribute in this case. There are four hybrid parts. The first two are the direct single-center contributions for $x=r$ of distributions $2s_a2p\sigma_a$, $2s_b2p\sigma_b$ and $1s_a2p\sigma_a$, $1s_a2p\sigma_a$. These cannot be accounted for by overlap integrals. In the CNDO and INDO methods, there appears only the $2s2p\sigma$ part. The other two result from two-center dipole parts of $2s_a2p\sigma_b$, $2s_b2p\sigma_a$ and $1s_a2p\sigma_b$, $1s_b2p\sigma_a$. They are in the third and fourth term of (2.6) for $x=r$. The sum of these five dipole parts reproduces the dipole moment of the wavefunction within 1% accuracy. This is not too surprising considering that (2.5b) is·defining the weighting factors. But it also shows that the neglect of

Table 3. Dipole moments (in Debye) of heteronuclear diatomics

		Ransil wavefunction [12]					STO basis [13]	
		M	Ch	This work	exact	exp.	CNDO	INDO
Li^+H^-	A	−2.71	−3.94	−4.77			−2.04	−2.19
	B			−1.20			−4.12	−4.01
	C			0.06				
	D			0.00				
	E			−0.02				
	F	−2.71	−3.94	−5.93	−5.92	−5.88	−6.16	−6.20
B^-H^+	A	−0.14	0.70	−1.81			−0.43	−0.46
	B			3.44			2.56	2.30
	C			−0.04				
	D			0.00				
	E			−0.02				
	F	−0.14	0.70	1.57	1.58		2.13	1.84
F^-H^+	A	1.01	1.74	0.25			1.09	1.30
	B			1.21			0.77	0.69
	C			−0.02				
	D			0.00				
	E			−0.01				
	F	1.01	1.74	1.43	1.44	1.74	1.86	1.99
C^-O^+	A	−0.94	−2.98	−1.03			−0.46	−0.40
	B			1.69			−0.18	−0.20
	C			−0.02				
	D			−0.04				
	E			0.00				
	F	−0.94	−2.98	0.60	0.59	0.12	−0.64	−0.60
Li^+F^-	A	−2.02	−3.16	−2.70			−5.82	−6.03
	B			−0.65			−2.08	−1.83
	C			0.02				
	D			−0.15				
	E			0.01				
	F	−2.02	−3.16	−3.47	−3.43	−6.6	−7.90	−7.86

A   charge part,
B   single-center $2s\,2p\sigma$ hybrid part,
C   single-center $1s\,2p\sigma$ hybrid part,
D   two-center $2s\,2p\sigma$ hybrid part,
E   two-center $1s\,2p\sigma$ hybrid part,
F   total dipole moment,
M   Mulliken,
Ch   Christoffersen.

higher-order terms in the weighting factors was not severe. Calculations with other Ransil wavefunctions confirm this result. For this accuracy, the contributions from D, i.e. the hybrid parts of the two-center $2s\,2p\sigma$, are in general not negligeable as can be seen from CO and LiF.

Neither the Mulliken, nor the Christoffersen approximation are in good agreement with the wavefunction's total dipole moment. This is true with or without hybrid parts. With regard to the CNDO and INDO charges, we feel

Table 4. Atomic occupation numbers in heteronuclear diatomics

A^+	B^-	Ransil wavefunction [12]							
		Mulliken				This work			
		$1s$	$2s$	$2p\sigma$	$2p\pi$	$1s$	$2s$	$2p\sigma$	$2p\pi$
Li		1.995	0.395	0.256		1.983	0.288	0.107	
	H	1.354				1.622			
B		1.999	1.808	1.169		1.996	1.810	0.888	
	H	1.024				1.305			
	F	1.999	1.946	1.284	2.000	1.999	1.934	1.124	2.000
H		0.771				0.943			
C		1.999	1.663	0.929	1.234	1.990	1.714	0.959	1.148
	O	1.999	1.865	1.545	2.766	1.994	1.858	1.485	2.852
Li		1.996	0.055	0.057	0.613	1.991	0.063	0.072	0.501
	F	1.999	1.943	1.950	3.387	1.998	1.970	1.906	3.499

that they may not be reliable, although the total dipole moments are often well reproduced.

For several reasons, we did not push this investigation farther at this time. Firstly, minimal basis sets are not producing good dipole moments, e.g. in CO and LiF. So the absolute value of these charge calculations is limited. Secondly, very few wavefunctions are published on polyatomics. A test in polyatomics would involve generating good wavefunctions. Thirdly, there is still some freedom in the polarization factors which concerns the functions μ' and v'. From (2.6) it can be seen that a particular type of function may be necessary, e.g. $2s_b$ and $2p\sigma_a$ for $x_{2s_a 2p\sigma_b}$, to ensure a proper united atom limit. For the usual internuclear distances, however, there is no constraint to fix the exponents. We feel that the most consistent scheme is one in which the basis functions of the MO's are used as μ' and v'. For example, it does not seem consistent to use $v' = 2p\sigma$ on hydrogen since this function is not in Ransil's basis set. Further study of this point is necessary.

In Table 4, we have compared the atomic occupation numbers for Mulliken's and our approximation. We observe in the hydrides a shift of charge from $2p\sigma$ of the hetero atoms to $1s$ of hydrogen as the main difference to Mulliken's analysis. CO is characterized by a shift of $2s$ and $2p\sigma$ charge from C to O and an opposite, but smaller shift of $2p\pi$ charge from O to C. This trend is over-emphasized in the Mulliken analysis. Yet opposite σ and π transfers cancel each other to a large extent. This effect is somewhat reduced by our polarization factors and leads to an increased overall charge transfer. LiF is bound primarily by a π-bond on top of an ionic σ bond. Transfer of the σ electron of Li is causing the polarity.

5. Electron Repulsion Integrals

Integral approximations for three- and four-center integrals were the starting point of the Mulliken approximation [14]. It was a gratifying idea to

Table 5. Error (%) of Mulliken and this work's integral approximations of two-center hybrid integrals for various ratios of orbital exponents and internuclear distances R (a.u.)

R	ζ_b/ζ_a	$(1s_A 1s_B\|1s_A 1s_A)$		$(2s_A 2s_B\|1s_A 1s_A)$		$(2p\sigma_A 2p\sigma_B\|1s_A 1s_A)$		$(2p\pi_A 2p\pi_B\|1s_A 1s_A)$	
		Mulliken	This work	Mulliken	This work	Mulliken	This work	Mulliken	This work
0	0.2	− 12	19	− 6	59	− 6	111	− 6	33
5		− 9	34	− 16	35	36	*504*	− 1	46
10		− 12	43	− 18	32	− 3	− 92	0.7	59
0	0.5	− 3	4	− 2	13	− 2	26	− 2	7
5		− 2	21	− 9	11	− 15	− 46	4	24
10		− 2	41	− 10	22	5	14	9	46
0	1	0	0	0	0	0	0	0	0
5		14	14	− 1	− 1	*5701*	*5701*	10	10
10		58	58	29	29	2278	2278	44	44
0	2	− 3	1	− 4	8	− 4	17	− 4	3
5		61	11	25	− 1	2	− 3	29	4
10		214	41	123	27	101	39	126	30
0	5	− 11	0.5	− 16	16	− 16	42	− 16	3
5		99	3	52	0.5	22	3	53	1
10		256	7	162	6	136	27	162	6

reduce multi-center integrals to two-center Coulomb integrals. Cisek [15] has compared the accuracy of various methods and proposed an expansion to reproduce multipole moments. Harris and Rein [16] also favored empirical adjustment so as to obtain best orbital coefficients for certain standard integrals which then could be used for other integrals.

We have considered the simplest two-center hybrid integrals $(1s_A 1s_B|1s_A 1s_A)$, $(2s_A 2s_B|1s_A 1s_A)$, $(2p\sigma_A 2p\sigma_B|1s_A 1s_A)$, $(2p\pi_A 2p\pi_B|1s_A 1s_A)$ and compared Mulliken's and our approximations for various ratios ζ_b/ζ_a with the exact values calculated with the formulas of Ruedenberg et al. [17]. The results are listed in Table 5. The errors of the Mulliken approximation are usually smaller than those of this work, if the orbital on center B is more diffuse than those on center A. We find our results improved over Mulliken's if the orbital on B is more contracted than those on A. The numbers in italics which indicate very large errors are at those distances where the exact integral is close to zero. Considering the fact that there seems to be not much gain in improved weighting factors, the question arises what the reason for this unsatisfactory behaviour could be. Certainly the influence of the location of distribution of the second electron is important. In this case the redistribution is to generate one-center integrals which are effectively overemphasizing the trend, namely to increase the integral value where the Mulliken approximation yields a too small value. This latter pattern is well pronounced in the table for all cases where the Mulliken approximation is closer to the exact values than ours, i.e. for $\zeta_b/\zeta_a < 1$. Also the neglect of the higher terms in (2.6) might be more crucial than in the single-electron case. We think that exchange integrals would be from symmetry more apt than hybrid integrals to an improved treatment with different weighting factors.

6. Conclusion

The calculations in this paper open the way to a new definition of atomic charges in molecules. Although the formulas were tested only in diatomics with Slater orbitals centered on the nuclei, a generalization is straightforward. A rotation of the results in a local coordinate system to a molecular coordinate system performed in the same way as in Pople's CNDO program would lead directly to atomic distributions in polyatomics. Also, there is no restriction of the formulas to Slater functions. The concepts hold also for Gaussian functions. Pure Gaussian functions would also allow in simple fashion to redistribute off-center orbital contributions. The same considerations hold also for approximations of other integrals. Electronic repulsion integrals are more sophisticated in structure and would need more care to guarantee a desired accuracy.

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