On the Charge Corrections of the Semi-empirical Parameters

in the Pariser-Parr-Pople Method I

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In an extension of the modified Pariser-Parr-Pople approximation the numerical values of the parameters W and γ have been varied with charge. Calculations have been made on formaldehyde, acrolein, formic acid, and the formate ion comparing different methods for the variation.

Recently a new scheme for the evaluation of semi-empirical parameters within the ZDO (zero differential overlap) approximation applied to unsaturated systems has been suggested.[1] Evaluation of numerical values of parameters appropriate to a series of atoms and atomic groups has later been performed.[2-11] The scheme is based on a systematic analysis of the ZDO approximation,[12] and the parameter values have been estimated through a least squares fit to experimentally determined molecular ionization potentials and singlet $\pi \to \pi^*$ transitions of chosen reference systems.

When these parameters are to be used in calculations on charged species, the problem arises if and how the parameter values should be varied with atomic charges. The same problem has been discussed earlier by Brown and Heffernan,[13] and by Karlsson and Mårtensson,[14] but as they have chosen different starting parameters, we have found it necessary to analyze the situation also within the present scheme.

In principle this problem is the same in ionic molecules and in neutral systems where the charge distribution is pronounced non-uniform. Previous calculations within this scheme have led to π-electron net charges as large as 0.5 electrons in neutral molecules. One bond for which the π-electron polarity is found to be extremely large, is the $C-O$ carbonyl bond.[5] Accordingly the present study has been confined to bonds involving carbon and oxygen, but the method can easily be extended to include other types of atoms.

METHODS

Two alternative assumptions have been made in this investigation:

Alternative 1. We assume that the parameter values evaluated within the scheme referred to above are valid for formally neutral atoms in accordance with the basic assumptions underlying the Pariser-Parr-Pople method. To obtain corrected results it is necessary even for the reference molecules to put in new parameters obtained by varying their values with charge according to certain functions given below. The calculations are then repeated to self-consistency, *i.e.* to a stage where the assumed input values of the atomic charges agree with the corresponding output values. This procedure leads to significant reductions of predicted atomic net charges, and in some cases the observed and calculated values of molecular properties do not agree as well as before.

Alternative 2. In this case we assume that the uncorrected parameters are valid for the atomic net charges predicted by their use on the chosen reference molecules. Accordingly the charge corrections are performed using the calculated charges in one reference molecule as basis for the variation. Otherwise the calculations are the same as in Alternative 1, *i.e.* the same functions for the variation of the parameters with charge are assumed, and the calculations are repeated to self-consistency. Values for the parameters appropriate to neutral atoms are calculated.

The parameters which have been varied in this investigation are the semi-empirically determined one-electron integrals W_μ and the one-center two-electron integrals $\gamma_{\mu\mu}$ taken from atomic spectral data. The assumed γ's have definite values for the neutral atom as well as for the anion and the cation. Thus when we in Alternative 2 assume, that the uncorrected parameters refer to the predicted atomic charges, we have to apply $\gamma_{\mu\mu}$ values corrected for charge. To obtain unchanged expectation values of the Fock operator for the test molecules (which is the real meaning of the expression that the uncorrected parameter values are valid) we must change W_μ in relation to the corrected γ value, so that $W_\mu + C\gamma_{\mu\mu}$ is unchanged, C being the coefficient in the Fock operator.

Functional relations. The next step is to determine the functions that give the variation of W_μ with charge. Two different functions for each atom have been used in both Alternative 1 and Alternative 2. They are denoted $F_1(\varrho)$ and $F_2(Z_{\text{eff.}})$, respectively.

In $F_1(\varrho)$ the differences between the valence state ionization potentials (IP) of the anion, the neutral atom and the cation have been used to estimate a variation in W_μ through a quadratic interpolation. Thus

$$W(\varrho) = W(0) - [IP(\varrho) - IP(0)] \qquad (1)$$

In $F_2(Z_{\text{eff.}})$ the variation of the valence state ionization potentials is considered as a function of $Z_{\text{eff.}}$, calculated according to Slater's rules. The ionization potentials for three isoelectronic atoms, *e.g.* B^-, C, and N^+ when the carbon parameters are to be determined, are taken as fixed points, and the values between are determined by quadratic interpolation. However, before making the interpolation, a correction for the difference in the positive charge of the

Table 1. Valence state ionization potentials for atoms and atomic ions, obtained from tables in Refs. 15 – 18 directly or by combination of values in these tables. All values in eV. It has only been possible to get values for the uncharged atom and for either the negatively or the positively charged atom. To get the third value in the series we have taken the IP value of an isoelectronic atom with different charge of the core and transformed this value according to Brown and Heffernan.[13] These transformed values are given in parentheses.

	C^- $t_1t_2t_3z^2 \rightarrow t_1t_2t_3z$ 0.62^a	C $t_1t_2t_3z \rightarrow t_1t_2t_3$ 11.22^a	$N+$ $t_1t_2t_3z \rightarrow t_1t_2t_3$ $28.72^{b,c}$ ($C+$ 22.98)
Keto	O^- $di^2di\pi^2\pi^2 \rightarrow di^2di\pi^2\pi$ $3.27^{a,c,d}$	O $di^2di\pi^2\pi \rightarrow di^2di\pi^2$ 17.91^c	$F+$ $di^2di\pi^2\pi \rightarrow di^2di\pi^2$ $39.90^{b,c,d}$($O+$ 34.20)
Ether	N^- $t_1^2t_2t_3z^2 \rightarrow t_1^2t_2t_3z$ 1.20^a(O^-1.44)	O $t_1^2t_2t_3z^2 \rightarrow t_1^2t_2t_3z$ 14.97^a	$O+$ $t_1^2t_2t_3z \rightarrow t_1^2t_2t_3$ $34.50^{a,b,c}$

[a] Ref. 15; [b] Ref. 16; [c] Ref. 17; [d] Ref. 18.

Table 2. The left hand side of the table gives valence state ionization potentials for isoelectronic series obtained from tables in Refs. 15 – 18 directly or by combination of values in these tables. Values in eV. The atoms in one series differ both in Z_{eff} and in core charge. Ionization potentials obtained after correcting for the difference in core charge are given in the right hand side of the table.

Carbon $t_1t_2t_3z \rightarrow t_1t_2t_3$						C, core charge 4		
	B^-	C	$N+$					
Core charge	3	4	5	$Z_{eff.}$		2.25	3.25	4.25
IP, eV	0.96^a	11.22^a	$28.72^{b,c}$	IP, eV		1.28	11.22	22.98
Keto oxygen $di^2di\pi^2\pi \rightarrow di^2di\pi^2$						O, core charge 6		
	N^-	O	$F+$					
Core charge	5	6	7	$Z_{eff.}$		3.55	4.55	5.55
IP, eV	$2.95^{a,d}$	17.91^c	$39.90^{b,c,d}$	IP, eV		3.54	17.91	34.20
Ether oxygen $t_1^2t_2t_3z^2 \rightarrow t_1^2t_2t_3z$						O, core charge 6		
	N^-	O	$F+$					
Core charge	5	6	7	$Z_{eff.}$		3.55	4.55	5.55
IP, eV	$1,20^a$	14.97^a	$36.77^{b,c}$	IP, eV		1.44	14.97	31.51

[a] Ref. 15; [b] Ref. 16; [c] Ref. 17; [d] Ref. 18.

core is made; see Ref. 13. This implies that IP for B^- is multiplied by $4/3$, IP for N^+ is multiplied by $4/5$, and IP for C is kept unchanged. When a net charge ϱ on a carbon atom is obtained by calculation with the PPP method, $Z_{\text{eff.}}$ for the atom is determined according to the relation $Z_{\text{eff.}} = 3.25 + 0.35\varrho$, and the difference between the IP value given by this $Z_{\text{eff.}}$ and the one corresponding to $Z_{\text{eff.}} = 3.25$ is used as the correction to the parameter W_μ. Thus for the carbon atom

$$W(Z_{\text{eff.}}) = W(3.25) - [\text{IP}(Z_{\text{eff.}}) - \text{IP}(3.25)] \tag{2}$$

In Tables 1 and 2 ionization potentials as well as effective nuclear charges for the three fixed points determining the parameters in the functions $F_1(\varrho)$ and $F_2(Z_{\text{eff.}})$ are given. The IP's are taken from tables in Refs. 15 – 18. The interpolation function for $F_1(\varrho)$ is assumed to be of the form:

$$\text{IP} = A_1\varrho^2 + B_1\varrho + C_1 \tag{3}$$

The correspondingly assumed relation for $F_2(Z_{\text{eff.}})$ is:

$$\text{IP} = A_2 Z_{\text{eff.}}^2 + B_2 Z_{\text{eff.}} + C_2 \tag{4}$$

The evaluated values of A, B and C based on the fixed points given in Tables 1 and 2 are presented in Table 3.

The numerical values of the two-electron one-center integrals appropriate to the anion, the neutral atom, and the cation of carbon and oxygen are presented in Table 4. Integral values corresponding to fractional electronic

Table 3. Coefficients in the functions $F_1(\varrho)$ and $F_2(Z_{\text{eff.}})$ given by eqns. (3) and (4) in the text.

Atom	Coeff. in $F_1(\varrho)$			Coeff. in $F_2(Z_{\text{eff.}})$		
	A_1	B_1	C_1	A_2	B_2	C_2
Carbon	0.58	11.18	11.22	0.9085	4.9433	-14.442
Keto oxygen	0.83	15.47	17.91	0.9590	6.6021	-31.983
Ether oxygen	3.00	16.53	14.97	1.507	1.323	-22.250

Table 4. One-center two-electron integrals for anion, neutral atom, and cation.

X	X^-		X^0		X^+	
	a.u.	eV	a.u.	eV	a.u.	eV
C	0.3718	10.12	0.4403	11.98	0.5088	13.84
O	0.6263	17.04	0.6947	18.90	0.7632	20.77

Table 5. The semi-empirical W_μ values used for uncharged atoms and standard distances ($R_{C=O}$= 1.22 A and R_{C-OH}= 1.35 A). The values in Alt. 2 are calculated as described in the text, the other values are taken from Refs. 5 and 6. For the dependence on both length see Refs. 5 and 6.

	W_C°	ΔW_C (O) (keto)			ΔW_C (O) (ether)	$W_O^\circ + \Delta W_O$(C) (keto)			$W_O^\circ + \Delta W_O$(C) (ether)
		Alt. 1	Alt. 2			Alt. 1.	Alt. 2		
			$F_1(\varrho)$	$F_2(Z_{eff})$			$F_1(\varrho)$	$F_2(Z_{eff})$	
a.u.	− 0.3617	− 0.0261	0.1674	0.0332	− 0.0033	− 0.7203	− 0.9619	− 0.7900	− 0.4109+0.0557
eV	− 9.84	− 0.71	4.56	0.90	− 0.09	− 19.60	− 26.17	− 21.50	− 11.18+ 1.51

charges have been estimated by linear interpolation using the data given in Table 4. The actual formula is:

$$\gamma(\varrho) = \gamma(0) + \varrho \times 0.0685 \text{ a.u.} \tag{5}$$

The W_μ values used, when the charge on the atoms is zero, are presented in Table 5.

RESULTS AND DISCUSSION

The procedures outlined above have been applied in a systematic study of ground state properties as well as electronic spectra of a series of unsaturated molecules containing C − O bonds. Both Alternative 1 and 2 have been used for the keto bonds, whereas only Alternative 1 for ether bonds, since the charges on the atoms in the ether bonds were small in the standard molecules used for the determination of the parameters.[6] For the purpose of comparison results obtained by the use of uncorrected parameters are included in the tables.

The compounds studied in the present work are formaldehyde, acrolein, formic acid, and the formate anion.

The quantity of main interest in the context of the present investigation is the predicted π-electron charge on the different atoms. This charge is not an observable quantity, but it determines the magnitudes of other quantities such as dipole moments and oscillator strengths.

It is furthermore of interest to examine the sensitivity of predicted values of other physical properties to changes in the parameter values due to charge corrections.

In Table 6 we present the predicted results for some ground state properties of the molecules considered. The main conclusion to be drawn from the data given in the table is that the predicted charges in Alternative 2 apart from those concerning the formate ion are almost the same as those obtained by the uncorrected parameters. Parameters corrected according to Alternative 1 reduce the predicted polarity in the π-electron distribution significantly. As charges of this kind are non-observable it is impossible to decide which set is the best one by comparison with experiment. However, ab initio calculations

Table 6. π-Electron net charges, bond orders, bond distances (in Å), and ionization potentials (in eV), predicted by use of different sets of charge-corrected parameters. For description of methods, see text.

Molecule		Uncorrected	Alternative 1		Alternative 2		Exp. values
			$F_1(\varrho)$	$F_2(Z_{eff.})$	$F_1(\varrho)$	$F_2(Z_{eff.})$	
Formaldehyde	net charge	C = 0.48	0.15	0.30	as for uncorrected		
		O = −0.48	−0.15	−0.30	(reference molecule)		
	bond order	0.879	0.989	0.954	»		
	bond dist.	1.207	1.187	1.193	»		1.208^a; 1.212^b
	IP	13.99	13.95	13.94	»		14.09^g
Acrolein	net charge	C_1 = −0.04	0.00	−0.01	0.00	−0.01	
		C_2 = 0.10	0.04	0.07	0.05	0.07	
		C_3 = 0.49	0.15	0.30	0.47	0.48	
		O_4 = −0.55	−0.20	−0.36	−0.52	−0.53	
	bond order	$C_1 - C_2$:0.957	0.956	0.956	0.961	0.959	
	bond dist.	1.345	1.345	1.345	1.344	1.344	1.345^c
	bond order	$C_2 - C_3$:0.272	0.285	0.285	0.271	0.274	
	bond dist.	1.468	1.466	1.466	1.468	1.468	1.470^c
	bond order	$C_3 - O_4$:0.808	0.940	0.897	0.825	0.816	
	bond dist.	1.219	1.196	1.204	1.217	1.218	1.219^c
	IP	10.77; 13.75	10.26; 13.60	10.47; 13.63	10.86; 13.52	10.80; 13.67	10.93^g; 13.2^g
Formic acid	net charge	C = 0.39	0.11	0.24	0.43	0.41	
		O = −0.53	−0.19	−0.35	−0.51	−0.53	
		OH = 0.13	0.08	0.11	0.09	0.11	
	bond order	C − O: 0.812	0.945	0.897	0.834	0.818	
	bond dist.	1.219	1.195	1.204	1.215	1.218	1.245^d; 1.217^e
	bond order	C − OH: 0.431	0.307	0.372	0.351	0.402	
	bond dist.	1.330	1.355	1.342	1.346	1.336	1.312^d; 1.361^e
	IP	10.90; 13.63	11.21; 13.89	11.02; 13.72	11.65; 13.69	11.20; 13.62	$*12.36^g$; 14.2^g
Formate ion	net charge	C = 0.36	−0.09	0.14	0.22	0.30	
		O = −0.51	−0.36	−0.42	−0.65	−0.58	Bond distances
		O^- = −0.86	−0.55	−0.72	−0.57	−0.72	in acetate ion ^{f}
	bond order	C − O: 0.819	0.764	0.811	0.650	0.737	
		$C - O^-$: 0.444	0.639	0.567	0.727	0.606	1.249 and 1.271
	IP	11.22; 13.81	4.90; 9.79	8.57; 12.50	5.29; 9.59	8.72; 12.41	

^{a} Ref. 23; ^{b} Ref. 24; ^{c} Ref. 25; ^{d} Ref. 26; ^{e} Ref. 27; ^{f} Ref. 28; ^{g} Ref. 29.
* A value 11.33 is in Ref. 29 assumed to be IP for a σ lone-pair electron.

with rather extended basis sets have almost reproduced the predicted π-electron charges for some other polar compounds studied by the same semi-empirical parameter scheme.[19-21] This does indicate rather strongly that Alternative 2 is the most realistic one for correcting our parameters due to non-uniform distribution of charges. The functions $F_1(\varrho)$ and $F_2(Z_{eff.})$ seem to yield comparable results for all the predicted quantities in this alternative.

The comparison between the different approaches is particularly interesting in the case of the formate ion. By using the uncorrected parameters we predict a charge distribution leading to two rather different oxygen atoms, and furthermore the two C − O bonds are found to be significantly different. The

Table 7. Transition energies and oscillator strengths predicted by use of different sets of charge-corrected parameters. For description of methods, see text.

| Molecule | Uncorrected | | | Alternative 1 | | | | | | Alternative 2 | | | | | | Exp. values |
| | | | | $F_1(\varrho)$ | | | $F_2(Z_{eff.})$ | | | $F_1(\varrho)$ | | | $F_2(Z_{eff.})$ | | | |
	Energy kK	Energy eV	Osc. strength f	Energy kK	Energy eV	Osc. strength f	Energy kK	Energy eV	Osc. strength f	Energy kK	Energy eV	Osc. strength f	Energy kK	Energy eV	Osc. strength f	eV
Formaldehyde	64.2	7.96	0.40	57.8	7.17	0.39	53.1	6.58	0.29	64.2	7.96	0.40	64.2	7.96	0.40	7.95[a]
Aerolein	50.5	6.26	0.70	48.8	6.05	0.70	49.0	6.08	0.71	51.7	6.41	0.79	50.8	6.30	0.75	6.41[a,b]
	61.5	7.63	0.10	61.5	7.62	0.04	61.2	7.59	0.07	61.0	7.57	0.06	61.2	7.59	0.06	
	69.6	8.62	0.18	65.5	8.12	0.37	66.8	8.29	0.27	69.4	8.61	0.10	69.6	8.63	0.15	
	87.8	10.88	0.13	86.6	10.74	0.16	87.1	10.79	0.15	86.0	10.66	0.17	87.2	10.82	0.14	
Formic acid	55.1	6.84	0.41	55.8	6.91	0.47	54.3	6.73	0.44	58.2	7.22	0.42	56.0	6.94	0.41	
	70.0	8.68	0.12	72.2	8.95	0.13	70.7	8.76	0.13	76.1	9.44	0.07	72.2	8.95	0.10	
Formate ion	55.2	6.85	0.44	48.3	5.99	0.69	48.7	6.03	0.52	50.0	6.20	0.51	50.1	6.21	0.46	
	71.3	8.84	0.11	66.4	8.23	0.13	67.2	8.33	0.15	68.4	8.47	0.13	68.3	8.47	0.12	

[a] Ref. 30; [b] Ref. 31.

same gross features are reproduced in Alternative 1, whereas Alternative 2 yields a structure which is more in conformity with two equivalent oxygen atoms and correspondingly two equivalent $C-O$ bonds. This conclusion is particularly valid if the $F_1(\varrho)$ function is used for correcting the parameters.

For the estimate of bond distances from calculated bond orders, we have used standard relations, two of them suggested previously,[5,22]

$$R_{\mu\nu}(C,C) \quad = 1.517 - 0.18\,p_{\mu\nu}\ \text{Å} \tag{6}$$

$$R_{\mu\nu}(C,O)_{\text{keto}} = 1.365 - 0.18\,p_{\mu\nu}\ \text{Å} \tag{7}$$

$$R_{\mu\nu}(C,O)_{\text{ether}} = 1.416 - 0.20\,p_{\mu\nu}\ \text{Å} \tag{8}$$

The constants in these relations are based on bond orders obtained by uncorrected parameters, and are accordingly strictly not valid for predictions of bond distances under Alternatives 1 and 2.

In all molecules, except for the formate ion, the changes are, however, so small that the relations may be assumed to be adequate. In the case of the formate ion, the bond orders calculated by the charge corrected parameters are drastically changed relative to the original ones. This implies that neither of the two formulae designed for estimates of $C-O$ bond lengths are applicable in this case.

In considering the bond orders for the formate ion given in Table 6, it is, however, worth noticing that by applying a factor of around 0.2 in front of the bond orders, we obtain, particularly in Alternative 2, a difference in the lengths of the two $C-O$ bonds, which is comparable to the observed one. One should, however, not put too much emphasis on this as the observed bonds refer to crystal data on the acetate ion.[28]

The predicted ionization potentials are in fair agreement with the measured ones, and the charge corrections do seem to introduce drastic changes in the predicted values only in the case of the formate ion. No experimental values are available, but the lowering of the predicted values by the charge corrections represents an expected change.

In Table 7 we present the influence on the predicted electronic transitions by the charge correction of the parameters. The experimental material available for comparison is scarce, but one might conclude that also in the treatment of the electronically excited states Alternative 2 is superior to Alternative 1 in the keto bonds.

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