Theoret. Chim. Acta (Berl.) 54, 145–156 (1980)

THEORETICA CHIMICA ACTA

Semiempirical Studies of Core-Electron Binding Energy Shifts

II. Self-Consistent Charge Calculations on Molecules Involving Boron and Carbon Atoms

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The inner-core binding-energy shifts (ΔBEs) of boron and carbon atoms in various chemical environments were studied by the semiempirical Self-Consistent Charge Molecular Orbital (SCC MO) method. The calculations are based on the initial ground state electrostatic potential model. The main feature of our approach is the empirical treatment of the coefficient relating ΔBEs with the orbital populations of the host atom and the Madelung energy term. These adjustable parameters absorb a large portion of relaxation energy. The so obtained results are in good agreement with experimental data. They are better than earlier CNDO/2 results obtained by using either ground state or relaxation potential models. Present results indicate that semiempirical methods like SCC MO are able to account for changes in $\Delta BE(1s)$ with a fair accuracy although the inner-shell electrons are not explicitly considered in the actual calculations.

Key words: ESCA spectroscopy – Inner-core levels, semiempirical calculation of ~

1. Introduction

The X-ray photoelectron spectroscopy (XPS) or ESCA proved useful in elucidating the gross electronic properties of molecules [1]. The shifts of inner-core electron energies are intimately related to formal atomic charges in molecules [2], nmr [3, 4] and Mössbauer phenomena [5], proton affinity of molecules [6] etc. The full *ab initio* treatment of ESCA chemical shifts involves the ground state calculation for each compound under consideration and the "hole" state calculation of the corresponding molecular ion for each atom taking part in the photoionization

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0040-5744/80/0054/0145/$02.40

process. Consequently, this approach is costly and highly impractical for large molecules of chemical or even biological interest. It is, therefore, desirable to have at one's disposal a simple and inexpensive but reliable semiempirical method which is applicable to large systems. The CNDO/2 theory does not serve the purpose because the calculated molecular charge densities are not very well correlated with inner-core energy shifts.[1] Thus, it is worthwhile to examine critically other semiempirical all-valence-electrons schemes.

The basic theory of the XPS process is well understood by now. Basch [8] and Schwartz [9] showed by theoretical consideration and by actual *ab initio* calculations that the 1*s*-electron energies are affected mostly by the average molecular electrostatic potential exerted on the site of the nucleus in question. The simple point charge approximation for the calculation of electrostatic potentials, introduced first by Siegbahn *et al.* [2] proved very useful in this respect. The basic formulas will be derived in this paper within the framework of self-consistent charge MO theory which fully employs the overlap integrals between the basis set functions. The second goal of the present work is to check the ability of the SCC MO wavefunctions to account for the changes of inner-core energies and to compare the quality of the resulting correlations with the available data obtained by other semiempirical methods. We consider in particular the shifts in 1*s*-electron energies for boron and carbon atoms in a wide variety of bonding situations. The complementary study of nitrogen, oxygen and fluorine atoms in different chemical environments is published elsewhere [10].

2. Outlines of the Calculation

The SCC MO method has been described elsewhere [11] and need not be discussed here. Rigorous treatment of inner-shell ionization requires the calculation of Hartree–Fock orbital energy values and the estimates of relativistic, correlation and reorganization corrections. The former can be neglected on the grounds that they are essentially atomic in nature. The correlation effect is supposed to be rather small for (1*s*) electrons because they are highly localized. A rough idea about the magnitude of the two-center exchange integrals is given by the squares of the corresponding overlap integrals. For example, the two-center integrals $\langle 1s_{N1} \mid 2s_{N2} \rangle^2$ and $\langle 1s_{N1} \mid 2p_{N2} \rangle^2$ in N_2 molecule are 0.0027 and 0.0078, respectively. Thus, the exchange contribution to the ESCA binding energy shifts may be disregarded in the first approximation. The reorganization energy plays an important role in XPS ionization processes. It may not be neglected and its relevance will be briefly discussed in a later section of this paper. If the relaxation energy is roughly constant, which is true for a series of related compounds of comparable size, then the shifts in 1*s* binding energies (ΔBEs) are linearly related to the changes of the intramolecular electrostatic potential

$$\Delta BE_{\mathrm{A}} = K\Delta V_{\mathrm{A}} + L \tag{1}$$

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[1] The discrepancies between the computed CNDO/2 point charges and the N(1*s*) energy shifts are quite dramatic. See e.g. Ref. [7].

where

$$V_A = \sum_B{}' [(Z_B - 2)/R_{AB}] - \langle 0|(1/r_A)|0\rangle \tag{2}$$

is the potential taken at the site of the ionized atom deliberately denoted by A. The origin of the coordinate system is placed at the nucleus A which is excluded from the summation. It is tacitly assumed that (1s) electrons are satisfactorily described by point charges which diminish the charge of the respective nucleus by two units. The one-determinantal ground state wavefunction is denoted by $|0\rangle$. It is formed by the valence-shell MOs Ψ_i which in turn are given in LCAO approximation

$$\Psi_i = \sum_\mu c_{i\mu}\Phi_\mu. \tag{3}$$

Employing the Mulliken approximation $\Phi_{\mu A}\Phi_{\nu B} = (1/2)S_{\mu\nu}(\Phi_{\mu A}^2 + \Phi_{\nu B}^2)$, Mulliken population analysis and the Taylor expansion of the operator $1/r_A$ in the course of calculation of two-center integrals $\langle\Phi_{\mu B}|(1/r_A)|\Phi_{\mu B}\rangle(\mu \in B, B \neq A)$ one obtains the final formula of the form

$$\Delta BE_A = k_1 Q_{2s}^A + k_2 Q_{2p}^A + k_3 \sum_B{}' (Z_B - 2 - Q_B)/R_{AB} + k_4 \tag{4}$$

where $Q_{2p}^A = Q_{2px}^A + Q_{2py}^A + Q_{2pz}^A$ and Q_μ is the orbital population

$$Q_\mu = P_{\mu\mu} + \sum_B \sum_\nu{}' P_{\mu\nu}S_{\mu\nu}.$$

Here $P\mu_a$ are the matrix elements of the conventional charge density–bond order matrix. The weighting factors k_i ($i = 1, 2, 3, 4$) are adjustable empirical parameters. A similar formula was developed by Schwartz *et al.* [12] within the framework of the CHDO/2 theory by using ZDO approximation. However, in their approach are $k_1 = k_2$ and $k_3 = 1$. We believe that this imposes unnecessary limitations for two reasons. Firstly, the constants k_1 and k_2 are related to the one-center integrals $\langle 2s_A|(1/r_A)|2s_A\rangle$ and $\langle 2p_{\alpha A}|(1/r_A)|2p_{\alpha A}\rangle$ ($\alpha = x, y, z$) which generally assume different values. They are equal only if Slater atomic orbitals possessing the same screening constants for s and p functions are employed. This is, however, not the case if the more refined atomic orbitals are used [13]. Secondly, the constants k_1, k_2, and k_3 should be treated as adjustable parameters which fit the experimental data in the best sense of the least-squares procedure. Then they absorb a large amount of the reorganization energy which is not explicitly taken into account otherwise.

The third term in formula (4) is called the Madelung term in analogy with a similar expression appearing in the theory of crystals and it will be abbreviated as M. Its significance in correlating ΔBEs is easily examined by switching the factor k_3 to zero ($k_3 \neq 0$ and $k_3 = 0$). Depending on the particular choice of the number of empirical parameters one obtains four models which are denoted by Q, $s + p$, $Q + M$ and $s + p + M$, the relation with the corresponding weighting factors being ($k_1 = k_2, k_3 = 0$), ($k_1 \neq k_2, k_3 = 0$), ($k_1 = k_2, k_3 \neq 0$) and ($k_1 \neq k_2, k_3 \neq 0$), respectively. It should be pointed out that only in the case of $k_1 = k_2$ the first two terms in formula (4) are contracted to the gross atomic charge $Q_A = Q_{2sA} + Q_{2pA}$

and ΔBEs are then related to the formal atomic charge of the atom A. Since the final formula involves only the initial ground state gross orbital populations and (or) the effective charges of atoms, the approach is usually referred to as the ground state potential method (GPM). Finally, it should be mentioned that only the gas phase is considered here. Thus, no experimental or theoretical problems of solid-state effects need concern us. All calculations are based on the best molecular geometries found in the literature.

3. Results and Discussion

3.1. Boron

The inner-core energy differences of boron atoms in various structural moieties span the range of 9 eV. The correlated values for Q, $Q + M$, $s + p$ and $s + p + M$ models are in fairly good agreement with experimental data (Table 1). The standard deviations are roughly 0.4 eV for all four approaches. Inclusion of the Madelung term diminishes the standard deviation by only 0.1 eV. Surprisingly enough, the $s + p$ model does not improve the quality of the correlation over the simple Q

Table 1. Comparison between the correlated and experimental 1s energies for boron atoms (relative to BF_3)[a]

	Method				
Molecule	Q	$Q + M$	$s + p$	$s + p + M$	Exp
BF_3	−0.3	−0.2	−0.3	−0.2	0
$B(OCH_3)_3$	−3.9	−4.2	−3.9	−4.2	−4.4
B_2H_6	−7.1	−7.0	−7.1	−7.0	−6.3
$B(CH_3)_3$	−5.9	−5.8	−5.8	−5.8	−6.5
BH_3CO	−7.8	−7.7	−7.8	−7.7	−7.6
$BH_3N(CH_3)_3$	−8.9	−9.3	−8.9	−9.3	−9.1
1,6-$C_2B_4H_6$	−7.5	−7.5	−7.5	−7.5	−7.4
1,5-$C_2B_3H_5$	−7.0	−6.9	−7.0	−6.9	−6.8
2,4-$C_2B_5H_7$					
1,7	−6.9	−6.7	−6.9	−6.7	−6.7
3	−7.1	−7.0	−7.1	−7.0	−7.2
5,6	−7.1	−7.6	−7.7	−7.6	−7.9
$B_2H_5N(CH_3)_2$	−7.2	−7.3	−7.2	−7.3	−7.5
B_5H_9					
1	−8.4	−8.3	−8.4	−8.3	−8.6
2–5	−7.2	−7.1	−7.2	−7.1	−6.7
BHF_2	−2.3	−2.2	−2.2	−2.2	−3.499[b]
BH_2F	−4.4	−4.4	−4.4	−4.4	−6.884[b]
BH_3	−6.8	−6.8	−6.7	−6.8	−10.223[b] −6.944[c]

[a] In eV units.

[b] *Ab initio* results of Ref. [14].

[c] Double-zeta calculations of Snyder and Basch, Ref. [15].

model, the standard deviations being virtually the same (0.4 eV). Analogously, the standard deviations for $Q + M$ and $s + p + M$ models are equal to 0.3. The largest discrepancy between the semiempirical results and the experimental values is found in diborane ($\sim$0.8 eV) which is most likely due to the special bonding characteristics of the three-center bonds involving hydrogens. It is gratifying that the results for coordinative compounds like BH_3CO and $BH_3N(CH_3)_3$ are in fine agreement with experiment. The general trend of the results presented in Table 1 follows the simple intuitive picture that the 1*s* binding energy is proportional to the net positive charge of the host atom. Thus, the largest binding energy is found in BF_3 where the boron atom bears the largest positive formal charge due to the high electronegativity of fluorine atoms. Since this level was chosen as a reference, the chemical shifts in core energy levels are negative. The one-center term Q gives the main contribution to the 1*s* binding energy. The small correction arises from the charges residing on the neighbouring atoms which enter in the Madelung term. Their negative charges will destabilize the 1*s* level of the ionized atom due to the Coulomb repulsion between the 1*s* electron and valence electrons of the neighbours. It follows that the Q and M terms exhibit opposite effects on the core electron. Furthermore, one could expect the linear relationship between the net charge of the atom under study and the Madelung term. Namely the electropositive host atom will make the nearest neighbour electronegative atoms negatively charged which diminishes the core electron binding energy because the contribution of the Madelung term is negative. Indeed, the linear least-squares fit method yields the formula $M_B = -0.805q_B + 0.025$ for boron. Here, the effective formal charges of boron atoms $q_B = Z_B - Q_B$ are used. If the compounds $B(OCH_3)_3$ and $BH_3N(CH_3)_3$ are excluded a nice straight line is obtained. This linear relationship is the reason behind the success of the simple Q model and we can safely state that the formal charge residing on the atom in question governs the changes in binding energies ΔBEs of the inner-shell electrons.

Inspection of Table 1 reveals that the intramolecular shifts in B_5H_9 and 2,4-$C_2B_5H_7$ are rather nicely reproduced by all four models. In order to check the ability of the SCC MO method to follow the changes along the series of related molecules we performed the calculations on BH_3 and its fluorinated derivatives. Since BH_3, BH_2F and BHF_2 were not used in the parametrization procedure the calculation provides a check of the SCC MO predictive power. The results are compared with the *ab initio* values of Schwartz and Allen [14] because experimental data are not available. The *ab initio* computations were carried on by employing a basis set which has approximately double-zeta quality. The $1s_B$ binding energies were obtained within the frozen orbitals approximation, i.e. by using Koopmans' theorem which identifies BE with the negative of the corresponding molecular orbital energy. One notices that the $1s_B$ binding energies of the multiply fluorinated molecules are shifted from BH_3 by amounts almost exactly a multiple of the shift for a simple fluorination. This conclusion holds for rigorous *ab initio* approach as well as for the semiempirical methods. The *ab initio* shifts seem to be too high which is probably a consequence of the somewhat inflexible basis set. Indeed, the Snyder and Basch *ab initio* calculation [15] of double-zeta quality yields the $1s_B$ binding energy for

BH_3 −6.944 eV relative to the reference BF_3 level. This is in good agreement with our prediction.

Next we shall compare our results with earlier semiempirical studies. Finn and Jolly [16] performed EHT and CNDO calculations on seven gaseous compounds involving boron atoms. In addition, Pauling's method for estimating boron atomic charges based on the electronegativity concept was applied too. All three methods exhibit large average errors if the Q model is used. They are ∓ 1.04 eV, ∓ 1.45 eV and ∓ 1.23 eV for EHT, CNDO and Pauling's method, respectively. The average errors are diminished to ∓ 0.83 eV, ∓ 1.21 eV and ∓ 1.20 eV if the Madelung term is included. However, the accuracy is still far from the desired. Our SCC MO results are significantly better as evidenced by the average errors ∓ 0.41 eV and ∓ 0.32 eV for Q and $s + p + M$ models, respectively. It should be pointed out that only the common molecules were taken into account for a comparison. The substantial average errors of EHT approach are not surprising because it is well documented by now that non-iterative EHT method exaggerates the intramolecular charge transfer leading to the large differences of the effective atomic charges. The Pauling's recipe for the determination of the formal atomic charges in molecules seems to be too crude for the calculation of ESCA shifts.

3.2. Carbon

The chemical shifts in C(1*s*) binding energies were studied for carbon atoms in 59 different chemical environments. They were measured relative to the reference level in CH_4 which is 290.8 eV [17]. Since the carbon atom assumes a wide variety of bonding situations due to the variation of its coordination number (2, 3 and 4) one could anticipate a large range of the chemical shifts. It is indeed as large as 11 eV. Surprisingly enough, it appears that the C(1*s*) binding energies are quite independent of the hybridization state of the parent atom. This is evidenced by the shifts in C_2H_6, C_2H_4 and C_2H_2 which are −0.2 eV, −0.1 eV and 0.4 eV, respectively. Although the binding energy exhibits a clear tendency to increase its value in passing from sp^3 to sp hybridization state this effect is very small. The dominating effect is the intramolecular charge transfer which is most pronounced in CF_4 where the atomic formal charge of carbon is 0.733 causing the largest chemical shift of 11 eV. Thus the simple intuitive picture that the larger positive charge of the atom suffering photo-ionization yields higher binding energies holds again. For this purpose it is constructive to consider the effect of multiple substitution on the C(1*s*) energy level shifts in CH_4. Let us focus our attention on the effect of a stepwise fluorination in a series of molecules of increasing electronic complexity: CH_4, CH_3F, CH_2F_2, CHF_3 and CF_4. One notices almost a uniform increase in experimental C(1*s*) binding energies along the series (Table 3). However, the increments are not exactly constant being 2.8 eV, 2.75 eV, 2.75 eV and 2.70 eV. The SCC MO calculations are compatible with the observed trend yielding the values 3.3 eV, 2.9 eV, 2.6 eV and 2.3 eV,[2] respectively. These shifts are parallel to the variation of the net C charges as obtained by the SCC MO method.

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[2] These values correspond to $s + p + M$ model but other models give similar results.

Table 2. Comparison between the correlated and experimental 1*s* energies for carbon atoms (relative to CH_4)[a]

	Method				
Molecule	Q	$Q + M$	$s + p$	$s + p + M$	Exp[b]
CH_4	−0.3	−0.2	−0.3	−0.2	0
C_2H_6	−0.1	0.0	0.0	0.1	−0.2
$C^*(CH_3)_4$	0.4	0.5	0.5	0.6	−0.4
C^*H_3CHO	0.8	0.6	0.7	0.5	0.6
$(C^*H_3)_2CO$	0.6	0.5	0.5	0.3	0.5
C^*H_3COOH	0.1	0.4	0.0	0.3	0.7
CH_3OH	1.9	2.0	2.0	2.0	1.75
$CH_3C^*H_2OH$	1.8	1.9	2.1	2.2	1.6
CH_3NO_2	2.4	1.8	2.3	2.0	2.08
CH_3Cl	1.2	1.1	1.3	1.3	1.6
CH_2Cl_2	2.3	2.1	2.4	2.3	3.1
$CHCl_3$	3.3	3.2	3.5	3.4	4.3
CCl_4	4.1	4.1	4.5	4.4	5.5
CH_3F	3.0	3.0	3.2	3.1	2.8
CH_2F_2	5.9	6.0	6.2	6.1	5.55
CF_3H	8.5	8.7	8.8	8.9	8.3
CF_4	10.8	11.1	11.0	11.2	11.0
C_2H_4	−0.2	−0.4	−0.0	−0.0	−0.1
C^*H_2CHF	1.1	0.9	1.1	0.8	0.18
$C^*H_2CF_2$	2.0	1.4	1.8	1.3	0.37
CH_2C^*HF	2.5	2.7	2.6	2.7	2.54
C^*HFCF_2	4.8	4.2	4.8	4.2	2.93
$CH_2C^*F_2$	5.1	5.4	5.2	5.4	5.14
$CHFC^*F_2$	5.2	4.9	5.7	5.3	5.28
$C^*H_3CH_2OH$	0.4	0.4	0.4	0.3	0.20
$C^*H_3CH_2F$	0.8	0.5	0.7	0.6	0.23
$C^*H_3CHF_2$	1.3	0.8	1.1	0.9	0.66
$C^*H_3CF_3$	1.8	1.0	1.4	1.0	1.11
$CH_3C^*H_2F$	2.8	2.7	3.1	3.2	2.43
$CH_3C^*HF_2$	5.5	5.7	5.8	6.0	5.09
$CH_3C^*F_3$	7.9	8.3	8.2	8.4	7.68
C_2F_6	9.5	9.3	9.6	9.3	8.91
C_6H_6	0.0	0.2	0.1	0.2	−0.50
C_6H_5F(C–F)	2.3	2.6	2.4	2.7	2.43
o-$C_6H_4F_2$(C–F)	3.0	3.2	3.0	3.1	2.87
m-$C_6H_4F_2$(C–F)	2.7	2.8	2.8	2.8	2.92
p-$C_6H_4F_2$(C–F)	2.7	2.8	2.7	2.8	2.74
p-$C_6H_4F_2$(C–H)	1.2	0.8	1.1	0.7	0.76
HCN	1.4	1.5	1.4	1.5	2.60
C_2H_2	−0.3	−0.2	−0.2	−0.2	0.4
OCC^*CO	1.5	1.0	1.0	0.6	0.8
C_3H_6	−0.1	−0.2	−0.1	−0.2	−0.3
$CHC^*HCHCHO$	0.5	0.6	0.4	0.5	−0.4
$C^*HCHCHCHO$	1.4	1.7	1.5	1.7	0.8
$CHC^*HCHCHNH$	−0.4	−0.2	−0.4	−0.3	−0.9

continued

Table 2—*Continued*

	Method				
Molecule	Q	$Q + M$	$s + p$	$s + p + M$	Exp[b]
$C*HCHCHCHNH$	0.4	0.6	0.4	0.5	0.1
C_2H_4O	1.9	2.0	1.9	2.0	1.8
$HCOOH$	4.3	4.7	4.3	4.6	5.0
CH_3C*OOH	4.4	5.0	4.1	4.6	4.7
H_2CO	2.9	3.1	2.9	3.1	3.3
CH_3C*HO	2.6	3.0	2.8	3.0	3.2
$(CH_3)_2C*O$	2.5	2.9	2.6	3.0	3.1
CO	2.7	3.0	4.3	4.3	5.3
CO_2	5.7	6.1	6.3	5.6	6.8
$OC*CCO$	3.4	3.5	3.3	3.4	4.2
CS_2	1.6	1.6	2.0	2.0	2.4
$C*H_3CN$[c]	0.9	0.7	0.8	0.6	—
CH_3C*N[c]	1.0	1.4	1.2	1.4	—
COS[c]	3.4	3.7	3.5	3.7	4.82

[a] In eV.

[b] Atoms involved in the photo-emission process are denoted by asterisk.

[c] Molecules not used in the parametrization procedure.

The differences in q_C charges between the subsequent members of the series $CH_4 \rightarrow CF_4$ are 0.22 $|e|$, 0.20 $|e|$, 0.18 $|e|$ and 0.16 $|e|$. It is interesting to compare present results with earlier *ab initio* computations. The electronic structure of the series $CH_4 \rightarrow CHF_3$ was studied by Schwartz *et al.* [18] who employed *a priori* wavefunctions of Ha and Allen [19] which in turn were based on the single-zeta basis set. The increments in C(1*s*) binding energy shifts calculated by the Koopmans' frozen orbitals approximation slightly increase along the series contrary to the experimental measurements, while the changes in q_C charges are constant (0.56 $|e|$). The same conclusion holds for ΔBE increments for the more refined calculations

Table 3. Comparison between the *ab initio*, semiempirical SCC MO and experimental ΔBE(1*s*) results and the net carbon charges for a series of fluorinated methanes[a]

	Increments in C(1*s*) binding energies					Increments in Mulliken charges of C atom		
	Ab initio			SCC MO				
Charges along the series	Koopmans[b]	Koopmans[c]	SCF[c]	present paper	Exp	*Ab initio*[b]	*Ab initio*[c]	SCC MO
$CH_4 \rightarrow CH_3F$	4.8	2.9	3.4	3.3	2.80	0.56	0.60	0.22
$CH_3F \rightarrow CH_2F_2$	4.9	3.2	3.0	2.9	2.75	0.56	0.47	0.20
$CH_2F_2 \rightarrow CHF_3$	5.0	3.3	3.4	2.6	2.75	0.56	0.34	0.18
$CHF_3 \rightarrow CF_4$	—	3.3	—	2.3	2.70	—	0.27	0.16

[a] Energies and net charges in eV and $|e|$ units, respectively.

[b] *Ab initio* results of Schwartz *et al.*, Ref. [18].

[c] *Ab initio* results of Basch *et al.*, Ref. [20].

of Bash *et al.* [20] who employed a flexible double-zeta atomic basis set and Koopmans' theorem. Their ΔSCF calculations yield fairly constant shifts too. This is somewhat surprising because the use of a double-zeta basis set in conjunction with sudden approximation ensures as a rule a good agreement with the experimental data. The ΔSCF calculations should be even more reliable. The source of the discrepancies between these theoretical treatments and measured values for the series $CH_4 \rightarrow CF_4$ is not known. It could be ascribed either to the calibration difficulties or to the imperfections of the applied theoretical methods, e.g. inadequacy of the neutral molecule basis set for the C(1*s*) hole state calculations in the ΔSCF approach. The fluorination of ethane and ethylene fits also the simple picture that the C(1*s*) binding energy is proportional to the net positive charge of the considered carbon atom. Thus the C(1*s*) levels are stabilized by the F substitution effect, the remote one being smaller by an order of magnitude. The multiple fluorination effect is roughly additive. It should be strongly pointed out that the simple proportionality between the net charge q_C and the binding energy shifts breaks down if substituent atoms belong to different rows of the system of elements. Comparison between the net q_C charges in CH_3F and CH_3Cl and the corresponding Δ*BE*s provides an excellent illustrative example. The ratio between the net charges in question is roughly 3 while $\Delta BE(CH_3F)/\Delta BE(CH_3Cl) \simeq 2$.

The predictive power of the SCC MO method was checked on CH_3CN and COS compounds which were not used in the parametrization procedure. According to the observed spectrum the splitting of the C(1*s*) levels in acetonitrile should be about 0.6 eV or less [21]. One observes that the theoretical estimates are 0.8 eV or less being thus close to the above requirement. The calculated value for COS is off by ~1 eV the measured value [22] which is not quite satisfactory. However, a survey of the results displayed in Table 2 shows that inter- and intra-molecular chemical shifts of the C(1*s*) energy levels are generally fairly well described by the SCC MO approach. It is of some importance to compare our results with other semiempirical work based on the GPM approach. We shall first consider the EHT calculations of Schwartz and Switalski [23]. They treated the electronic charge distributions in molecules as continuous ones and consequently the average values of the $(1/r)$ operator were rigorously calculated over the EHT MOs. The studied carbon atoms encompass 32 different chemical environments. If the molecules CO, CS_2, CH_3Cl, CH_2Cl_2, $OHCl_3$ and CH_4 are included in the correlation the standard deviation is 1.4 eV which is significantly less favourable than our results for $s + p + M$ model which has the standard deviation of 0.6 eV. Similar calculations were performed by Schwartz for a smaller set of representative molecules employing the CNDO/2 method [24]. The standard deviation was 1.3 eV which is slightly better than the EHT value but still far away from the SCC MO calculations. These findings are not surprising because the EHT method exaggerates the intramolecular charge transfer while the CNDO/2 charge distributions exhibit some shortcomings which were at some length discussed earlier [11], and it is not to be repeated here. One has to point out, however, that the Δ*BE* shifts in fluorinated methanes and benzenes are described by two different scales in the CNDO/2 approach. These scales disagree by 0.9 eV [25]. On the other hand the present SCC MO results refer to a common single scale although a wide range of compounds such as perfluorohydrocarbons, heterocyclics, aliphatic and aromatic molecules are considered.

The question arises how the methods which take into account only the initial state may yield reasonable results particularly if it is known that reorganization energy usually assumes values in the range between 10–20 eV for the first-row atoms. It appears that the reorganization energy can be to a large extent related to the ground-state charge distribution. The molecular relaxation energy may be expressed as a sum of two terms [26]

$$E_A(r) = E_A(\text{contr}) + E_A(\text{flow}), \tag{5}$$

where $E_A(\text{contr})$ is the part of the relaxation energy arising from the contraction of the atomic orbitals placed on the host nucleus A. It is a consequence of the increased electron-nuclear attraction. The second term $E_A(\text{flow})$ is structurally dependent and comes from the electron charge distribution in the whole molecule. Snyder [27] has shown that $E_A(\text{contr})$ is linearly related to the net charge of the parent nucleus before the photoionization

$$E_A(\text{contr}) = Cq_A + C_2. \tag{6}$$

Thus the contraction energy is absorbed in the empirical parameters k_1, k_2 and k_4 in our approach. The reorganization energy $E_A(\text{flow})$ is to some extent described by the adjustable weighting factor k_3. This is the reason behind the ability of the adopted theoretical method to tackle different families of molecules on an equal footing (i.e. by the formula (4)). It should also be added that the SCC MO provides fairly good charge distributions as evidenced by the extensive calculations of molecular quadrupole moments [11]. This is concomitant with the present quite successful calculation of XPS energy level shifts.

4. Conclusion

We found that the semiempirical SCC MO method in conjunction with electrostatic potential model is useful in correlating (1*s*) binding energy shifts in a large number of molecules involving boron and carbon atoms. It quite successfully accounts for the variation in *BE* as a function of the changes in chemical environment. The present results are significantly better than the previous EHT and CNDO/2 ones. The lowest standard deviations were obtained by the four-parameter $s + p + M$ model but the two-parameter Q model has also a satisfactory performance indicating that the electronic charge distributions in molecules are reasonably well described by the SCC MO wavefunctions. In addition, it seems that the large amount of the relaxation energy is absorbed in the adjustable parameters k_i ($i = 1, 2, 3, 4$). This feature allows a treatment of the widely different compounds by the same empirical formula. It is worth mentioning that *BE* shifts as calculated by the SCC MO method proved useful in discussing the problem of intramolecular hydrogen bonding and keto-enol tautomerism in 1,3-diketones [28]. The calculated inner-shell levels were good enough to assign the experimental data. Thus, the criticism that the semiempirical methods are unable to tackle ESCA shifts because they do not explicitly consider inner-core electrons [29] and use arbitrary definitions of formal atomic charges [30] seems to be unwarranted. However, some caution has to be exercised whenever the semiempirical approach is applied to molecules possessing unusual bonding characteristics. Excellent examples which prove this point are given by B_2H_6 and COS where the results are off by ~ 1 eV. Furthermore, one has to bear in mind that the electrostatic potential model given in the point charge approximation has always to be taken "cum grano salis". It provides a convenient treatment, but lacks the proper theoretical basis because any static arrangement of point charges is unstable according to Earnschaw's theorem.

Acknowledgement. This work was financially supported in part by the Self-managing Authority for Scientific Research of the SR of Croatia and also by the National Science Foundation (Grant No. F6F 006y).

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Received May 10, 1979/August 22, 1979