

CCA-810

YU ISSN 0011-1643

539.13

Original Scientific Paper

## On the Electrostatic Calculation of the ESCA Chemical Shifts

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Received November 2, 1973

The electrostatic formula for the calculation of the ESCA chemical shifts is developed within the framework of the INDO approximation and by using Taylor expansion of the  $1/r$  operator. The INDO wavefunctions were employed for the calculation of the 1s electron binding energy changes in some characteristic organic molecules. It was shown that the electrostatic formula based on the point charge approximation works quite well and that the inclusion of the polarized charge cloud does not improve the results to any significant extent.

Recently discovered<sup>1</sup> X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) proved to be a very useful and powerful tool for studying the electronic structure of molecules. The method is based on the fact that the energy of the »inert« inner shell electrons exhibits different shifts in different chemical environments as measured from the reference molecule. The proper quantum mechanical *a priori* treatment includes the relativistic effects\*\*, the change in correlation energy between the molecule and its ion, the reorganization energy of the ion's orbitals *etc.* Fortunately, many of these effects are small or constant and can be consequently neglected. For example, the relativistic effects for the first row atoms have<sup>2</sup> order of magnitude 1 eV while the change in correlation energy should not significantly exceed the same amount<sup>3,4</sup>. In spite of the fact that the reorganization energy, caused by the relaxation of molecular orbitals upon core ionization, is considerable, it is well established by now that the use of Koopman's theorem enables one to make fairly reliable estimates of the changes in inner core binding energies<sup>5,6</sup>. These calculations, however, require an *ab initio* approach and therefore they are either too expensive or not permissible for most molecules of chemical interest. Thus many simple empirical and semi-empirical methods have been developed which correlate the inner shell binding energy shifts with the average potential at the nucleus site. The potential is usually calculated in the point charge approximation

$$\Delta BE \approx \Delta V = kq_A + E_M + I \quad (1)$$

where  $q_A$  is the gross atomic charge residing on the nucleus in question A,  $E_M$  is the Madelung energy arising from the electrostatic interaction between

\*\* The inner shell electrons are close to the nucleus and their velocity is by no means negligible when compared with the velocity of light.

an 1s electron and the charges of all other atoms B ( $B \neq A$ ):  $E_M = \sum_{B \neq A} q_B / r_B$ . Further,  $k$  and  $l$  are adjustable empirical parameters. The semiempirical methods mentioned above differ in the definition of the formal atomic charges  $q_A$  and the way of their calculation. The electronic charge distribution could be calculated by using one of the current semiempirical methods like CNDO/2<sup>7</sup>, IEHT<sup>8</sup> or perhaps the electronegativity equalization procedure<sup>9</sup>. The eqn. (1) can be rationalized by the parallel changes between the average electrostatic potential at the nucleus\* and the *ab initio* vertical ionisation potentials obtained within the »sudden« or »frozen orbitals« approximation<sup>10</sup>. It gives very good correlation for ESCA chemical shifts for the molecules involving first row atoms. In this paper we discuss in some detail the quantum mechanical origin of the empirical eqn.(1). In particular, we shall develop the approximate electrostatic potential formula at the INDO<sup>11</sup> level of sophistication by using Taylor expansion of the operator  $1/r$  around the nucleus in question. The ESCA chemical shifts of carbon atoms in some characteristic molecules will be discussed in terms of the INDO first order density matrix elements and the various contributions of the terms in the Taylor series  $1/r$ .

#### OUTLINE OF THE PROCEDURE

The 1s electrons are considered as highly localised and nonpolarised cores which diminish the respective nuclear charges by two units. The average electrostatic potential energy of the 1s carbon electron placed in the origin of the coordinate system is of the form (in a. u.):

$$E_p(C) = - \sum_{A \neq C} (Z_A - 2) / r_A + \langle 0 | 1/r | 0 \rangle \quad (2)$$

where  $Z_A$  is the atomic number of the nucleus A and  $\langle 0 | 1/r | 0 \rangle$  denotes the average value over the ground state determinant formed by the valence shell molecular orbitals  $\psi_i$  and C stands for the carbon atom in question. The molecular orbitals are linear combination of atomic orbitals  $\Phi_\mu$ :  $\psi_i = \sum_{\mu} c_{i\mu} \Phi_\mu$ . The average value of the  $1/r$  operator can be expressed by the charge density-bond order matrix elements  $P_{\mu\nu} = \sum_{\mu} \sum_{\nu} c_{i\mu} c_{i\nu}$  and the integrals over atomic orbitals

$$\langle 0 | 1/r | 0 \rangle = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \langle \Phi_\mu | 1/r | \Phi_\nu \rangle \quad (3)$$

Since the way of the summation is quite arbitrary, the eqn.(3) can be written in the more convenient form

$$\begin{aligned} \langle 0 | 1/r | 0 \rangle = & \sum_{\mu}^C P_{\mu\mu} \langle \Phi_\mu | 1/r | \Phi_\mu \rangle + \sum_{A \neq C}^A \sum_{\mu} P_{\mu\mu} \langle \Phi_\mu | 1/r | \Phi_\mu \rangle + \\ & 2 \sum_{A \neq C}^A \sum_{\mu < \nu} P_{\mu\nu} \langle \Phi_\mu | 1/r | \Phi_\nu \rangle \end{aligned} \quad (4)$$

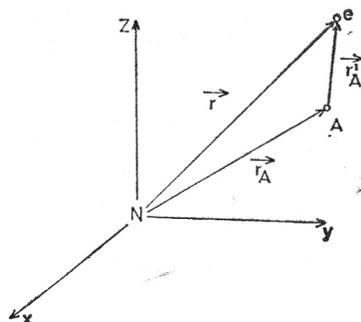
where we, in addition, neglected all integrals involving the product  $\Phi_\mu \Phi_\nu$  if both atomic orbitals are not placed on the same atom, concomitant with the INDO approximation. The one-center integrals are readily calculated once

\* properly calculated by evaluating all many-center integrals.

the basis set functions are chosen. Employing Slater type orbitals one obtains for the first row atoms

$$\langle \Phi_{\mu}^C | 1/r | \Phi_{\mu}^C \rangle = (Z_C - S_C)/4 \quad (5)$$

where  $S_C$  is the screening constant. One observes that the one-center integrals do not depend on the angular part of the atomic orbitals. The two-center integrals appearing in the eqn.(4) are calculated by using the Taylor expansion of the  $1/r$  operator around the carbon atom by using transformation of the coordinates  $\mathbf{r} = \mathbf{r}_A + \mathbf{r}_A'$  (Fig. 1).



$$\begin{aligned} 1/|\mathbf{r}_A + \mathbf{r}_A'| &= 1/r_A - (1/r_A^3) \mathbf{r}_A \cdot \mathbf{r}_A' + (3/2 r_A^5) [x_A' y_A' x_A y_A + x_A' z_A' x_A z_A + \\ &+ y_A' z_A' y_A z_A] - (1/2 r_A^5) [(x_A')^2 (r_A^2 - 3x_A^2) + (y_A')^2 (r_A^2 - \\ &- 3y_A^2) + (z_A')^2 (r_A^2 - 3z_A^2)] + \dots \text{higher terms} \end{aligned} \quad (6)$$

By using formulae (5) and (6) one obtains

$$\begin{aligned} E_p(c) &= (Z_c - S_c) P_{cc}/4 - \sum_{A \neq C} \{ q_A / r_A - (10/\sqrt{3}) (Z_A - S_A) r_A^3 \} \sum_{\alpha} \alpha_A P_{2s^A} P_{2p_{\alpha}^A} \\ &- (6/(Z_A - S_A)^2 r_A^5) [r_A^2 \sum_{\alpha} P_{2p_{\alpha}^A} P_{2p_{\alpha}^A} - 3 \sum_{\alpha} \alpha_A^2 P_{2p_{\alpha}^A} P_{2p_{\alpha}^A}] + (126/(Z_A - \\ &S_A)^2 r_A^5) \sum_{\alpha < \beta} \alpha_A \beta_A P_{2p_{\alpha}^A} P_{2p_{\beta}^A} \} \end{aligned} \quad (7)$$

where  $P_{AA} = \sum_{\mu} P_{\mu\mu}^A$ ,  $q_A$  is the formal charge on the atom A:  $q_A = Z_A - P_{AA} - 2$  and greek letters  $\alpha$  and  $\beta$  run over the coordinates  $x$ ,  $y$  and  $z$ . The first two terms of the eqn.(7) form the electrostatic formula (1) based on the point charges. It is interesting to examine whether the additional terms give better agreement with experiment. The calculations are performed in the local coordinate systems which are by convention parallel with the frame of the molecular coordinate axes. Since the orientation of axes in space is arbitrary, the expression (7) has to be invariant to the rotation of the coordinate system. One can easily find out that eqn.(7) meets this requirement. Let us for example consider the term  $\sum_{\alpha} \alpha_A P_{2s^A} P_{2p_{\alpha}^A} = x_A P_{2s^A} P_{2p_x^A} + y_A P_{2s^A} P_{2p_y^A} + z_A P_{2s^A} P_{2p_z^A}$ . We have to recall first that the elements of the charge den-

sity-bond order matrix  $P_{\mu\nu}$  are formed by the coefficients of the molecular orbitals which in turn are vectors in the Hilbert subspace spanned by the basis set of atomic orbitals. The  $P_{\mu\nu}$  elements transform contravariant while the atomic orbitals transform covariant upon the rotation of the coordinate system. Secondly, we observe that the coordinates  $\alpha_A$  ( $\alpha = x, y$  and  $z$ ) have the same angular dependence as p orbitals. Thus, in the new coordinate system the relevant quantities, denoted here with double prime, are of the form

$$(P_{2s^A 2p^A})'' = \sum_{\beta} O_{\alpha\beta}^{-1} P_{2s^A 2p^A}^A \quad (\alpha_A)'' = \sum_{\gamma} O_{\alpha\gamma} \gamma_A$$

where  $O$  is the matrix which relates the coordinates of the rotated and initial coordinate system. Now we can straightforwardly check the rotational invariance of the term

$$\begin{aligned} \sum_{\alpha} \alpha_A P_{2s^A 2p^A}^A (\sum_{\alpha} \alpha_A P_{2s^A 2p^A}^A)'' &= \sum_{\alpha} \sum_{\beta} \sum_{\gamma} O_{\alpha\beta}^{-1} P_{2s^A 2p^A}^A O_{\alpha\gamma} \gamma_A = \sum_{\beta} \sum_{\gamma} \delta_{\alpha\gamma} \\ \gamma_A P_{2s^A 2p^A}^A &= \sum_{\beta} \beta_A P_{2s^A 2p^A}^A \text{ q. e. d.} \end{aligned}$$

The invariance of the other terms in the formula (7) is easily checked along the same lines.

#### RESULTS AND DISCUSSION

The INDO calculations are performed on a series of organic molecules. The experimental shifts in 1s energies of the carbon atoms are correlated with the average electrostatic energy calculated at various levels of approximation:

$$\Delta BE(C) = k E_n + 1 \quad (8)$$

where  $n = 1, 2, 3$ . The results are presented in Table I. The first formula  $E_1$  includes only the effect of the point charges.

TABLE I

Comparison between the experimental ESCA chemical shifts and those calculated by various levels of approximation of the electrostatic formula for carbon atoms\*.

Molecule	Exp.	$E_1/eV$	$E_2/eV$	$E_p/eV$
$C_6H_6$	-0.40	1.97	+2.05	1.35
$C_3H_6$	-0.23	0.67	0.69	0.15
$C_2H_6$	-0.20	-0.15	-0.18	-1.07
$CH_4$	0.00	0.60	0.55	-0.48
$C_2H_2$	0.04	4.63	4.55	4.25
$CH_3OH$	1.90	1.44	1.45	0.69
$CH_3F$	2.80	2.46	2.46	1.80
$HCOOH$	4.99	4.09		4.19
$CO$	5.40	7.18	7.22	7.08
$CO_2$	6.84	7.54	7.41	7.67
$CHF_3$	8.30	6.08	6.10	6.27
$CF_4$	11.00	7.87	7.95	8.53

\*  $E_1 = (Z_N - S_N) P_{NN}/4$ ;  $E_2 = E_1 + [10/\sqrt{3} (Z_A - S_A) \sum_{\alpha} \alpha_A P_{2s^A 2p^A}^A]$  and  $E_p$  is given by the formula (7), see text.

The next expression  $E_2$  involves the anisotropy of the atomic charge distribution called usually the hybridisation term  $P_{2s}^A P_{2p}^A$ .  $E_p$  stands for the full expression given by the eqn.(7). The quality of the correlations is reflected in the standard deviations 2.00, 1.97 and 1.88 eV for  $E_1$ ,  $E_2$  and  $E_3$  respectively. We notice slight improvement by including more terms in the Taylor expansion. This improvement is however not decisive since the standard deviation of  $E_p$  is still high and the agreement with experiment is more qualitative than quantitative. It is hard to say whether the only moderate agreement with experiment should be ascribed to the inadequacy of the electrostatic approach or to the failure of the INDO method to give more reliable charge distribution in molecules. However, in view of good correlations obtained with the electrostatic formula by using wave functions calculated by other methods even for atoms involving lone pairs<sup>8</sup> it seems that INDO still leaves much to be desired. Finally, we conclude that the point charge formula (1) works good enough and that the inclusion of terms involving polarisation of atomic charge density does not improve significantly the agreement with experiment.

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## SAŽETAK

## O elektrostatskom izračunavanju ESCA-kemijskih pomaka

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Koristeći Taylorov razvoj potencijala  $1/r$  dobivena je približna formula za elektrostatsko izračunavanje ESCA-kemijskih pomaka. Formula je konzistentna s aproksimacijama koje sadržava semiempirijska metoda molekularnih orbitala — INDO. Uzimajući u obzir samo prva dva člana Taylorova razvoja dobiva se formula koja odgovara aproksimaciji točkastih naboja atoma u molekuli. Izvedeni su INDO-računi na nizu karakterističnih ugljikovodika i pokazano je da uključivanje prostorne raspodjele elektronskog naboja kao i njegove polarizacije ne doprinosi znatno boljem slaganju s ESCA-kemijskim pomacima dobivenima eksperimentalnim putem.

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Primljeno 2. veljače 1973.

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