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Short Communication

NDDO MO Calculations

IV. Correlation of *K*-Shell Binding Energy Shifts

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Siegbahn's potential model as extended by Ellison *et al.* is used with density matrix elements calculated by the NDDO/2 procedure, to correlate the *K*-shell binding energy shifts of C, N and O atoms in a few molecules containing only the first-row atoms. The correlation is not superior to that obtained with the CNDO/2 method when only the monopole term is retained in calculating the Madelung potential energy. However, the results are in excellent agreement with experiment when the two-parameters model including the dipole and quadrupole terms is used.

Key words: *K*-shell binding energies

1. Introduction

X-ray photoelectron spectroscopy has become a powerful technique for studying molecular electronic structure and as a means of testing the quality of calculated molecular wave functions [1–3]. Several different approaches have been used to interpret the observed changes in core binding energies of particular atoms in different chemical environments, the so-called ESCA chemical shift. These vary in their sophistication, from simple correlation with the charge on the atom involved to direct calculation of the core binding energies [1–5]. A simple and popular model proposed by Siegbahn *et al.* [1] employs an expression of the type (1) for correlating the shifts.

$$E_B = kq + V + l. \qquad (1)$$

In this equation q is the net charge on the atom under consideration, V is the potential due to electronic and nuclear charges on all other atoms. k and l are obtained by a least-squares procedure. This expression has been used in conjunction with CNDO/2 and INDO MO methods to predict the *K*-shell shifts for carbon,

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nitrogen and oxygen atoms in various molecules [1], the average errors being around 1 eV for C and N shifts and 0.5 eV for O shifts.

Ellison *et al.* [6–7], while deriving the theoretical justification for this model, proposed two improvements: a two-parameter model in which the interaction of the core with the $2s$ and $2p$ orbitals on the same atom are treated individually, and inclusion of the dipole and quadrupole terms in calculating the extra-atomic Madelung potential term V. Within the CNDO/INDO framework the correlation improved considerably when the two-parameter model was used but the inclusion of dipole and quadrupole terms had little effect.

In the present series of papers [8–10] we have been considering in detail the potential of a modified version of Roby's NDDO MO [11, 12] method. Since the calculated wavefunctions provided a faithful representation of their *ab initio* counterparts, we have employed NDDO MO wavefunctions to correlate the K-shell binding energy shifts for Cl, N and O using the Siegbahn's model as extended by Ellison *et al.*

2. Method of Calculation

In the present model the shift in the K-shell binding energies as the electronic environment changes is written as

$$E_{\mathrm{A}} = -k_s^{\mathrm{A}}\Delta q_{\mathrm{A}s} - k_p^{\mathrm{A}}\Delta q_{\mathrm{A}p} - \Delta V_{\mathrm{A}} + l, \tag{2}$$

where $\Delta q_{\mathrm{A}s} = q_{\mathrm{A}s} - q_{\mathrm{A}s}^0$ represents the differences between $2s_{\mathrm{A}}$ orbital electron population in the given molecule and in the reference molecule, and $\Delta q_{\mathrm{A}p}$ is the corresponding difference between $2p_{\mathrm{A}}$ populations. k_s^{A} and k_p^{A} are parameters representing combinations of atomic Coulomb and exchange interaction between $1s$ core and $2s$ and $2p$ orbital electrons on atom A respectively. l is a least-squares parameter to correct for errors inherent in the model. $\Delta V_{\mathrm{A}} = V_{\mathrm{A}} - V_{\mathrm{A}}^0$ is the difference in the Madelung potential energy at A arising from monopoles, dipoles, quadrupoles etc. centered on all atoms other than A, where

$$V_{\mathrm{A}} = V_{\mathrm{M}} + V_{\mathrm{D}} + V_{\mathrm{Q}}. \tag{3}$$

The monopole term:

$$V_{\mathrm{M}} = \sum_{n \neq \mathrm{A}} (q_n - Z_n^{\mathrm{core}})/R_{n\mathrm{A}}. \tag{4}$$

The dipole term:

$$V_{\mathrm{D}} = -5 \sum_{n \neq \mathrm{A}} \sum_{T} P_{ST}^{(n)} T_{n\mathrm{A}}/(3^{1/2}\zeta_n R_{n\mathrm{A}}^3). \tag{5}$$

The quadrupole term:

$$V_{\mathrm{Q}} = 3 \sum_{n \neq \mathrm{A}} \sum_{T} \sum_{U} P_{\mathrm{TU}}^{(n)}(3T_{n\mathrm{A}}U_{n\mathrm{A}} - R_{n\mathrm{A}}^2\, \delta_{TU})/(2\zeta_n^2 R_{n\mathrm{A}}^5). \tag{6}$$

In the above equations,

$$q_n = \sum_{r}^{n} P_{rr} \tag{7}$$

represents the total charge on atom n. T and U are the Cartesian components x, y, z. T_{nA} is the Tth coordinate of atom n relative to atom A. $P_{ST}^{(n)}$ is the $2s - 2p_T$ density matrix element. $P_{TU}^{(n)}$ is the $2p_T - 2p_U$ density matrix element. ζ_n is the STO exponent on atom n.

Calculations were performed using both the single parameter model ($k_s^A = k_p^A$ in Eq. 1) and the two-parameter model. In one set of calculations only the monopole term was included and in another V_D and V_Q terms were also included in evaluating V_A.

The density matrix elements over Löwdin symmetric orthogonalized orbitals were evaluated using the NDDO/2 scheme, the calculational details of which are described in [10]. While calculating the dipole and quadrupole terms it was assumed that the MO coefficients correspond to an STO basis rather than to the STO-3G basis actually employed in calculating the wavefunction. Also the exponents for C, N and O atoms were taken as 1.57, 1.92 and 2.23 respectively, values close to the Clementi-Raimondi s and p exponents [13] used in obtaining the STO-3G functions.

3. Results and Discussion

The $1s$ binding energies were calculated using the various models for C, N and O atoms. The experimental values [1, 14] and the ones using a 2-parameter model including dipole and quadrupole terms are presented in Table 1. The average errors are also indicated in each case.

Table 1. Calculated $1s$ ESCA shifts for C, N and O in some selected molecules using the two-parameters model with dipole and quadrupole terms

Carbon ($1s$)[a]			Nitrogen ($1s$)[b]			Oxygen ($1s$)[c]		
Molecule	ESCA shift calculated	Exp.[d]	Molecule	ESCA shift calculated	Exp.[d]	Molecule	ESCA shift calculated	Exp.[d]
CH_4	0.15	0.00	NH_3	−0.11	0.00	H_2O	−0.32	0.00
C_2H_4	0.28	−0.10	N_2	4.26	4.35	CO_2	1.76	1.44
C_2H_2	−0.15	0.40	CH_3NH_2	−0.33	−0.45	CH_3OH	−0.53	−0.80
C_2H_6	0.05	−0.10	$N\underline{N}O$	6.93	6.95	O_2	3.57	3.84
CH_3OH	1.84	1.90	$\underline{N}NO$	2.97	3.05	N_2O	1.53	1.54
CH_2O	3.44	3.30	σ[e]	0.08		σ[e]	0.24	
$CH_3\underline{C}HO$	2.71	3.20						
$\underline{C}H_3CHO$	0.61	0.60						
CO_2	7.10	6.84						
σ[e]	0.24							

[a] $K_s = -6.984$, $k_p = -15.564$, $l = 0.151$

[b] $K_s = -11.112$, $k_p = -7.695$, $l = -0.114$

[c] $K_s = -21.206$, $k_p = -21.301$, $l = -0.317$

[d] = Ref. [1, 14]

[e] = Average error

The single parameter model with only the monopole term yields correlations with average errors around 1 eV in all three cases, similar to the results obtained with CNDO and INDO methods. On going over to the two-parameter model, the results, though not quite unsatisfactory, are still inferior to those obtained by the CNDO method at the same level of calculation. There has been a noticeable reduction in the average errors for O and N shifts but little in the case of C shifts.

The inclusion of the additional terms in V_A, however, has resulted in a steep fall in the average error. The corresponding two-parameter model has an average error of only 0.24 eV for C and O and 0.08 eV for N.

Although the number of molecules considered for N and O shifts is rather small, the excellent performance of NDDO/2 in the prediction of C shifts is indisputable. These results represent some of the best predictions of ESCA chemical shifts for C, N and O atoms by any MO method without the inclusion of valence relaxation effects. Taken together with the supposition of Ellison *et al.* [6] that the dipole and quadrupole terms in the extra-atomic Madelung potential will be important when calculated using better wavefunctions, it may be concluded that the NDDO/2 wavefunctions indeed provide faithful representations of *ab initio* functions.

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References

1. Siegbahn, K., Norbing, C., Johansson, G., Hedman, J., Heder, P. F., Hamrin, K., Gelius, V., Bergmark, T., Werme, L. O., Manne, R., Baer, Y.: ESCA applied to free molecules. Amsterdam: North-Holland, 1969
2. Basch, H., Snyder, L. C.: Chem. Phys. Letters **3**, 333 (1969)
3. Schwartz, M. E.: Chem. Phys. Letters **5**, 50 (1970)
4. Hendrichson, D. N., Hollander, J. M., Jolly, W. L.: Inorg. Chem. **8**, 2642 (1969)
5. Schaefer, H. F.: The electronic structure of atoms and molecules. Reading, Mass.: Addison-Wesley, 1972
6. Ellison, F. O., Larcom, L. L.: Chem. Phys. Letters **13**, 399 (1972)
7. Ellison, F. O., Larcom, L. L.: Chem. Phys. Letters **10**, 580 (1971); Schwartz, M. E.: Chem. Phys. Letters **6**, 631 (1970); **7**, 78 (1970)
8. Chandrasekhar, J., Mehrotra, P. K., Subramanian, S., Manoharan, P. T.: Theoret. Chim. Acta (Berl.) **41**, 243 (1976)
9. Mehrotra, P. K., Chandrasekhar, J., Manoharan, P. T., Subramanian, S.: Theoret. Chim. Acta (Berl.) **41**, 257 (1976)
10. Chandrasekhar, J., Mehrotra, P. K., Subramanian, S., Manoharan, P. T.: Theoret. Chim. Acta (Berl.), in press
11. Roby, K. R.: Chem. Phys. Letters **11**, 6 (1971)
12. Roby, K. R.: Sinanoğlu, O.: Intern. J. Quantum. Chem. **IIIS**, 223 (1969)
13. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
14. Davis, D. W., Hollander, J. M., Shirley, D. A., Thomas, T. D.: J. Chem. Phys. **52**, 3295 (1970)

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