Semiempirical Studies of Inner-Core Energy Levels. IV. ESCA Shifts of Nitrogen Atoms in Different Chemical Environments by the SCC-MO Method

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The binding energy shifts of the 1s levels of nitrogen atoms in 15 different bonding situations are calculated by the self-consistent charge molecular orbital (SCC-MO) method employing an electrostatic potential model in the point charge approximation. The standard deviation of the obtained correlation is ~ 0.5 eV, which is substantially better than the earlier CNDO/2 GPM and RPM results. The scatter of the correlated values is diminished to roughly 1/3 of the previous CNDO/2 results. The merits and shortcommings of the electrostatic potential model are briefly discussed. It is concluded that the present approach provides a useful tool for studying ESCA shifts in large molecules of biochemical interest.

1. Introduction

XPS or ESCA spectroscopy is useful in discussing the electronic structure of molecules in the gaseous and solid states [1, 2], the properties of polymers [3], chemi- and physisorption phenomena [4, 5], homogenous catalysis [6] etc. The rigorous treatment of the photoionization process is rather advanced. It involves Δ SCF calculation for each ionized atom in a molecule, with inclusion of relativistic and correlation corrections. Thus it is necessarily confined to small systems. If larger compounds are to be studied, one has to resort to semiempirical theories of chemical bonding. It is gratifying that all valence-electron schemes at the EHT and CNDO/2 levels of approximation used in conjucation with the electrostatic model reproduce the major features of the ESCA chemical shifts [7, 8]. However, the standard deviations of the emirical correlations obtained with these two methods are sometimes unsatisfactorily high. The ESCA shifts of nitrogen atoms in different chemical environment represent such a case [7, 9]. It is the aim of this work to show that better results can be obtained if the self-consistent charge molucular orbital (SCC-MO) method is employed. This is of some importance because the ability of the semiempirical methods to account for the changes in ESCA shifts was recently questioned on the grounds that the inner-shell electrons are not explicitly included in the computational procedures [10].

2. Method

A discussion of the SCC-MO method was given previously [11] and is not to be repeated here. We have shown [12] that ESCA chemical shifts are related to the orbital populations of the host atom via the equation

$$\Delta \mathrm{BE}_{\mathrm{A}} = k_1 Q^{\mathrm{A}}_{2\mathrm{s}} + k_2 Q^{\mathrm{A}}_{2\mathrm{p}} + k_3 \sum_{\mathrm{B}}{}' (Z_{\mathrm{B}} - 2 - Q_{\mathrm{B}})/R_{\mathrm{AB}} + k_4 , \quad (1)$$

where the ionized atom in a molecule is denoted by A. The gross orbital population are given by $Q^{\mathrm{A}}_{2\mathrm{s}}$ and $Q^{\mathrm{A}}_{2\mathrm{p}_\alpha}$ $(\alpha = x, y, z)$ with

$$Q^{\mathrm{A}}_{2p} = Q^{\mathrm{A}}_{2p_x} + Q^{\mathrm{A}}_{2p_y} + Q^{\mathrm{A}}_{2p_z} .$$

The adjustable parameters k_i $(i = 1, 2, 3, 4)$ are determined by fitting the experimental inner-core energy level shifts using the least-squeres technique. The third term in (1) is called the Madelung potential in analogy with a similar expression appearing in solid state theory. In the following it

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will be abreviated by M. Depending on the number of parameters and their interrelations one obtains four models which are denoted by Q, $s+p$, $Q+M$ and $s+p+M$, 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. Since the final formula involves only the ground-state orbital populations and (or) net atomic charges, the method belongs to the ground state potential (GPM) approach. It should be finally pointed out that all results correspond to molecules in the gaseous state. The computations are based on the best molecular geometries available in literature.

3. Results and Discussion

The chemical shifts of the nitrogen (1s) energy levels relative to the N_2 molecule were calculated for 15 different compounds. The results are displayed in Table 1. The experimental data span a range as large 12.3 eV. The largest N(1s) binding energy was found in ONF_3. This is a consequence of the large electronegativity of fluorine and oxygen atoms. By comparing the relevant figures in Table 1 one notices the good quality of the SCC-MO results. The destabilizing effect of the methyl substitution on the N(1s) level in NH_3 is nicely reproduced. The binding energy is decreasing along the series NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ due to the increased negative charge of the nitrogen atom. The nonequivalent nitrogen atoms in NNO are clearly distinguished. The correlated chemical shift for ONF_3 is in good agreement with experiment. The relatively large deviation found for the reference molecule is somewhat disturbing, but this compound is clearly different from the rest of the studied substances. Although the core hole is localized on one nitrogen atom [13] like in other molecules, a quite different reorganization energy could be anticipated for a diatomic molecule compared with other polyatomic compounds. Other empirical or semiempirical calculations failed to predict N(1s) chemical shifts in a satisfactory manner. Jolly et al. [9] have studied N(1s) binding energies for the same series of molecules as we did. The formal atomic charges calculated by Pauling's electronegativity method [14] gave a large scatter with standard deviation of 2.02 eV. This is unacceptably high and it seems that the Pauling atomic charges are not accurate enough for quantitative estimates of ESCA chemical shifts. The CNDO/2 results given within the framework of the GPM approach exhibit also a large standard deviation of 1.65 eV, which is somewhat diminished by inclusion of the Madelung term. However, the present SCC-MO results are substantially better as evidenced by the standard deviations of 0.58, 0.60, 0.50 and 0.49 (in eV) for the Q, $Q+M$, $s+p$, $s+p+M$ models, respectively. Furthermore, the CNDO/2 method predicts a slight increase in the N(1s) binding energies along the series $NH_3 \rightarrow (CH_3)_3N$, contrary to the experimental observations and SCC-MO results. It is interesting to mention that we did not get any significant improvement in N(1s) shifts by taking into account the Madelung term. In fact, we found a good linear relation between SCC-MO net charges of the host nitrogen atoms and the corresponding Madelung potentials. This finding explains the good performance of the simple Q model. Thus the increased accuracy is a consequence of better estimates of effective ground state atomic charges and is not due to the use of a larger set of flexible parameters. The EHT method exhibits appreciable standard deviations for N(1s) shifts too [8, 15]. To summarize, we can say that the scatter of the correlated inner-core N(1s) energy levels is diminished to roughly 1/3 if the SCC-MO method is applied.

Table 1. Comparison between the correlated and experimental 1s energies for nitrogen atoms (relative to N_2 molecule)[a].

Molecule Method	Q	$Q+M$	$s+p$	$s+p$ $+M$	Exp.
$(CH_3)_3N$	− 5.0	− 4.8	− 4.9	− 4.7	− 5.2
$(CH_3)_2NH$	− 4.3	− 4.0	− 4.2	− 4.3	− 5.0
CH_3NH_2	− 4.6	− 4.5	− 4.7	− 4.7	− 4.8
NH_3	− 4.3	− 4.1	− 4.5	− 4.6	− 4.3
N_2H_4	− 3.7	− 3.5	− 3.7	− 3.7	− 3.8
HCN	− 3.7	− 3.6	− 3.2	− 3.1	− 3.1
$(CN)_2C_2(CN)_2$	− 3.9	− 3.8	− 3.4	− 3.4	− 2.8
N*NO	− 1.3	− 1.2	− 0.8	− 1.1	− 1.3
N_2	− 1.4	− 1.3	− 0.8	− 0.8	0
$C_6H_5NO_2$	1.9	2.1	1.8	1.9	1.75
CH_3NO_2	2.3	2.4	2.2	2.2	2.18
N_2F_4	2.5	2.6	3.2	3.2	2.4
NN*O	2.1	2.2	1.7	1.8	2.6
NF_3	4.5	4.6	5.0	5.1	4.3
ONF_3	7.2	7.3	7.1	7.1	7.1

[a] in eV units.

The question arises whether the better performance of the SCC-MO method for N(1s) shifts is

Table 2. Standard deviations of the various electrostatic potential methods (in eV units).

Family of compounds	Standard deviations					
	CNDO/2 Method		SCC-MO Method			
	GPM	RPM	Q	$Q + M$	$s + p$	$s + p + M$
C (1s) shifts						
fluoromethanes	0.3^{a}	0.7^{a}	0.3	0.3	0.5	0.5
fluoroethanes	0.6	0.3	0.5	0.4	0.6	0.6
fluoroethylenes	0.7	0.6	1.1	0.8	1.0	0.7
F (1s) shifts						
fluoromethanes	0.2	—	0.4	0.3	0.2	0.2
fluoroethanes	0.4	—	0.5	0.3	0.4	0.4
fluoroethylenes	0.3	—	0.3	0.4	0.2	0.3
total of 11 different boron nuclei	1.0^{b}	0.5^{b}	0.4	0.3	0.4	0.3
total of 31 different carbon nuclei	1.1^{a}	0.7^{a}	0.8	0.7	0.7	0.6
total of 11 different nitrogen nuclei	2.9^{a}	2.3^{a}	0.5	0.5	0.4	0.4
total of 10 different oxygen nuclei	2.4^{a}	1.2	0.6	0.5	0.5	0.6
total of 11 different fluorine nuclei	0.2^{c}	—	0.3	0.3	0.2	0.2

[a] CNDO/2 ground state potential (GPM) and relaxation potential (RPM) calculations, see [7].

[b] CNDO/2 transition potential calculations, see [18].

[c] CNDO/2 ground state potential calculations, see [17].

fortuitous or gives generally more reliable electron charge distributions in molecules than the two aforementioned semiempirical schemes. For this purpose we made an analysis which is presented in Table 2. The standard deviations of our present and previous SCC-MO results [12, 16] are compared with the corresponding entities obtained by the CNDO/2 studies of ESCA shifts. The available CNDO/2 results were obtained in the GPM approximation [7, 17] and the relaxation potential model (RPM), which takes into account explicitly the reorganization energy [7]. For the set of 11 boron nuclei we used the results of the GPM and transition potential model (TPM) CNDO/2 calculations of Goscinski et al. [18]. Perusal of the relevant data shows that the SCC-MO method provides correlations with smaller standard deviations. This conclusion holds with very few exceptions. In fact, only when particular families of molecules are considered the CNDO/2 approach yields better results. For example, the CNDO/2 GPM model is more succesful in fluoromethanes while the CNDO/2 RPM method yields lower standard deviations in fluoroethanes. However, the SCC-MO calculations provide a better overall picture being substantially more reliable for nitrogen and oxigen nuclei. There are several reasons for the good performance of the method adopted in this paper. Firstly, the rather complicated inner-shell photoionization phenomenon can fortunately be reduced to Coulomb interactions described by the electrostatic potential without significant loss of information. Secondly, expectation values of the $1/r$ operator are not exceedingly sensitive on the finer details of molecular wavefunctions. This conclusion is supported by the results of several ab initio calculations, which show that $\langle 0 | 1/r | 0 \rangle$ values are little affected by the changes of the basis sets or by the inclusion of massive CI [19]. In other words, relatively accurate values of the $1/r$ operator can be obtained by using approximate wavefunctions. It seems that the point charge approach is quite satisfactory in this respect, although $1/r$ is strictly speaking a one-electron operator. Similar insensitivity was observed for second moments and the related diamagnetic part of the magnetic susceptibility which can also be calculated in the point charge approximation [20, 21]. Finally, it appears that SCC-MO wavefunctions reproduce fairly well gross features of the charge redistribution accompanying formation of chemical bonds as evidenced by the numerous calculations of molecular quadrupole moments [11]. One concludes that the SCC-MO procedure yields better results for one-electron properties than the semiempirical methods based on the ZDO approximation, indicating that the overlap integrals play an important role in the theory of chemical bonding.

A comment on the relaxation energy is in place here. It has appreciable values which sometimes exceed the range of the ESCA chemical shifts. However, the present results and the earlier calculations [12, 16] provide conclusive evidence that a large portion of the relaxation energy is absorbed in adjustable parameters k_i ($i = 1, 2, 3, 4$) for the first row atoms. Thus it appears that the effect of the final state can in most cases be incorporated in the charge distribution of the ground state. Indeed, SCC-MO equivalent core and transition potential calculations for nitrogen yield virtually the same standard deviations (~ 0.5), which means that on average there is no improvement. In other words, it is generally more important to use a method which provides reliable ground state atomic charges than to include the effect of electron reorganization. It is, however, important to stress that the latter should be explicitly taken into account if molecules with special structural characteristics are considered. Consequently, the improvement which is occasionally obtained by the inclusion of the transition potential in CNDO/2 calculations reflects more remedy of some of the internal inconsistencies involved in the applied semiempirical scheme than the influence of the final ionic state. This is concomitant with our conclusion reached by the calculations of molecular quadrupole moments [11]. The unsatisfactory performance of the CNDO/2 approach is actually not surprising because it is known that this scheme has no proper theoretical structure while for example the IEHT method does have [22, 23].

It was argued that the electrostatic potential model is ill defined because any assignment of charge to particular atoms in a molecular environment is arbitrary and strongly dependent on the employed basis set [24, 25]. Our results suggest that the ESCA energy shifts are satisfactorily reproduced within the all-valence electron semiempirical framework if a reliable method is used and if a reasonable population analysis is consistently applied. Since the employed SCC-MO procedure is easily executed even for large molecules, it provides a convenient tool for studying ESCA shifts in complexes, macromolecules and compounds of biochemical and pharmacological interest. One should, however, always bear in mind that electrostatic potential method(s) (GPM, RPM or TPM), particularly in the point charge approximation, only simulate the proper a priori treatment and that physical significance can not be attached to the notion of point charge.

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[1] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, ESCA Applied to Free Molecules, North Holland, Amsterdam 1969.

[2] U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, Phys. Scrip. **2**, 70 (1970); D. T. Clark and D. M. J. Lilley, Chem. Phys. Letters **9**, 234 (1971).

[3] J. Delhalle, J. M. Andre, S. Delhalle, J. J. Pireaux, R. Candano, and J. J. Verbist, J. Chem. Phys. **60**, 595 (1974); D. T. Clark and A. Dilks, J. El. Spectry. Rel. Phenom. **11**, 225 (1977), and the references cited therein.

[4] A. F. Carley, R. W. Joyner, and M. W. Roberts, Chem. Phys. Letters **27**, 580 (1974).

[5] B. Gumhalter, J. Phys. C. Sol. State Phys. **10**, L219 (1977); B. Gumhalter, Surf. Science **80**, 459 (1979).

[6] C. Andersson and R. Larsson, Chem. Scripta **11**, 140 (1977), and the references cited therein.

[7] D. W. Davis and D. A. Shirley, J. El Spectry. Rel. Phenom. **3**, 137 (1974).

[8] M. E. Schwartz and J. D. Switalski, J. Amer. Chem. Soc. **94**, 6298 (1972).

[9] P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, Inorg. Chem. **10**, 378 (1971).

[10] I. R. Levin, Molecular Spectroscopy, John Wiley & Sons, New York 1975, p. 319

[11] J. E. Bloor and Z. B. Maksić, Mol. Phys. **22**, (1971); ibid., **26**, 397 (1973).

[12] Z. B. Maksić and K. Rupnik, Croat. Chem. Acta **50**, 307 (1977).

[13] L. C. Snyder, J. Chem. Phys. **55**, 95 (1971).

[14] L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell Univ. Press, 1960.

[15] M. E. Schwartz, J. D. Switalski, and R. E. Stronski, Electron Spectroscopy, D. A. Shirley ed., North Holland, Amsterdam 1972, p. 605.

[16] Z. B. Maksić and K. Rupnik, Theor. Chim. Acta **54**, 145 (1980).

[17] D. W. Davies, M. S. Banna, and D. A. Shirley, J. Chem. Phys. **60**, 237 (1974).

[18] H. Siegbahn, R. Medeiros, and O. Goscinski, J. El. Spectry. Rel. Phenom. **8**, 149 (1976).

[19] S. Rothenberg and H. F. Schaefer, III, Mol. Phys. **21**, 317 (1971); B. J. Rosenberg and I. Shavitt, J. Chem. Phys. **63**, 2162 (1975); C. F. Jackels and E. R. Davidson, J. Chem. Phys. **63**, 4672 (1975).

[20] Z. B. Maksić and N. Mikac, Chem. Phys. Letters **56**, 363 (1978); J. Mol. Structure **44**, 255 (1978).

[21] Z. B. Maksić and N. Mikac, Mol. Phys. **46**, 455 (1980).

[22] D. B. Cook, P. C. Hollis, and R. McWeeny, Mol. Phys. **6**, 553 (1967).

[23] F. Driessler and W. Kutzelnigg, Theoret. Chim. Acta **43**, 307 (1977).

[24] K. Wittel and S. P. McGlynn, Chem. Rev. **77**, 745 (1977).

[25] H. A. Bent, J. Chem. Phys. **54**, 824 (1971).