Core-Level Binding Energy Shifts and the Average Quantum Mechanical Potential at a Nucleus from CNDO Theory

Maurice E. Schwartz

Contribution from the Department of Chemistry and the Radiation Laboratory,[1]
University of Notre Dame, Notre Dame, Indiana 46556.
Received March 2, 1972

Abstract: The use of changes of the average potential at a nucleus to measure the changes of core electron binding energies (ΔBE) is considered for CNDO wave functions. The often used equation $\Delta\mathrm{BE} = Kq + V + L$ is a direct consequence of the analysis. Here q is the charge of the atom whose core electron is considered, V is the potential at that atom due to charges at other atoms, and K and L are *well-defined* quantities, instead of empirically adjusted ones as in previous studies. Earlier applications are considered in light of this analysis, from which only C 1s ΔBE's are seen generally to correspond to the potential changes and from which the deficiency of CNDO in describing the electronic structures is inferred. Further calculations using the potential produce only modest gains in accuracy, as is also the case for calculations in which both q and V are allowed adjustable parameters. Discussion and suggestions for further work are given.

In the rapidly developing field of X-ray photoelectron spectroscopy (XPS or ESCA) there have been many useful correlations of shifts in core binding energies with various quantities, as reviewed in previous publications.[2-4] One of the more common has been the point-charge potential model[2]

$$\Delta\mathrm{BE}_A = kq_A + V + l \qquad (1)$$

where k and l are adjustable parameters, q_A is the calculated charge at the atom A of interest, and V is the potential at A due to calculated point charges at other atoms.

$$V = \sum_{B\neq A} q_B/R_{AB}$$

From a more fundamental viewpoint it has been shown[5,6] that ΔBE's depend linearly (with slope near unity) on the change of the potential at the nucleus on which the core orbital sits, when the potential is the quantum mechanical average calculated from an accurate *ab initio* SCF–MO wave function. The contribution to the potential from the core MO's at the home nucleus is insensitive to environment, and potential changes are the same as changes in the potential with the local core contribution removed. Furthermore, because the core MO's at other nuclei screen their home nuclei completely as far as the potential at the given nucleus is concerned, these other core MO's can be ignored in the potential calculation if their home nuclear charges are appropriately reduced. Thus one need only consider the potential at atom A due to valence electrons

$$\Phi_{\mathrm{val}} = -2\sum_{i\neq \mathrm{core}} \langle\phi_i|1/r_A|\phi_i\rangle + \sum_{B\neq A} Z_B^*/R_{AB} \qquad (2)$$

where ϕ_i are doubly occupied MO's, r_A is an electronic position from A, and Z_B^* are the effective reduced nuclear charges. Detailed analysis[6] suggested that the observed $\Delta\mathrm{BE} - \Delta(\Phi_{\mathrm{val}})$ relationship should be general. Since Φ_{val} can be calculated from valence-only MO theories, there thus exists a possibility of finding core ΔBE's by explicit consideration of valence electrons only. We have investigated this approach using the extended Hückel theory,[7] and Davis, *et al.*,[8] have recently published similar work on fluorinated methanes and benzenes, using CNDO theory.

In this paper we discuss a ΔBE expression which is a direct consequence of using the valence potential Φ_{val} of eq 2 to measure ΔBE's when the CNDO approximation[9] is systematically applied[10] and which has the same form as eq 1. In contrast to previous applications of eq 1, however, the quantities corresponding to k and l are well defined. We consider previous applications in light of this fact and present some further related calculations and discussions.

Substitution of LCAO expansions for the ϕ_i in eq 2 and application of the CNDO approximation[9,10] separate the electronic part of Φ_{val} into 1- and 2-center parts. The 1-center part reduces[10] to $-K_AP_A$, where P_A is the valence electron population at A, and K_A is the nuclear attraction integral of a valence STO at A for nucleus A, with value ζ_A/n_A for an STO of principal quantum number n_A and orbital exponent ζ_A. Great simplification also occurs for the 2-center parts if all relevant nuclear attraction integrals for nucleus A are given a value $1/R_{AB}$. This choice is dictated by the requirement that Φ_{val} be invariant to arbitrary orientations of the basis functions,[10] as in the formulation of CNDO;[9] and it

---

[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-833. This work has been partially supported by the Petroleum Research Fund, administered by the American Chemical Society, Grant No. 5122-A6.

[2] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

[3] 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 Publishing Co., Amsterdam, 1969.

[4] (a) J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, 3, 193 (1970); (b) J. M. Hollander and D. A. Shirley, *Annu. Rev. Nucl. Sci.*, **20**, 435 (1970).

[5] H. Basch, *Chem. Phys. Lett.*, **5**, 337 (1970).

[6] M. E. Schwartz, *ibid.*, 6, 631 (1970).

[7] M. E. Schwartz, *ibid.*, 7, 78 (1970), and further work, *J. Amer. Chem. Soc.*, in press.

[8] D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **56**, 671 (1972).

[9] J. A. Pople and G. A. Segal, *ibid.*, 44, 3289 (1966). Appendix E of ref 3 discusses CNDO and its previous use for ESCA studies.

[10] M. E. Schwartz, J. D. Switalski, and R. E. Stronski, *Proc. Int. Conf. Electron Spectrosc.*, 605 (1972).

seems to introduce negligible error.[8] The resulting 2-center electronic contributions are $-\Sigma_{B \neq A} P_B/R_{AB}$, where the P_B are valence electron populations at the other atoms B. Since $q_B = Z_B^* - P_B$, combination of these electronic terms with the nuclear contributions in eq 2 produces the simple result

$$\Phi_{val} = -K_A P_A + V$$

which can be written in terms of the charge *via* addition and subtraction of $K_A Z_A^*$

$$\Phi_{val} = K_A q_A + V - K_A Z_A^* \qquad (3)$$

The form of eq 1 is directly obtained by *assuming* $\Delta BE = \Delta\Phi_{val}$ and using a reference potential $\Phi_{val}{}^R$ from which shifts are measured

$$\Delta BE = K_A q_A + V + L \qquad (4)$$

where the identification $L = -K_A Z_A^* - \Phi_{val}{}^R$ is made.

Previously[2] k in eq 1 was identified with the Coulomb repulsion integral (k_{AC}) between a core and valence electron at atom A, rather than the nuclear attraction integral K_A which enters the potential, but in practice it was treated as an adjustable parameter. Table I summarizes K_A, k_{AC}, and the least-squares k values for C, N, O, F, and S atoms.[2] While K_A and k_{AC} are similar, only for C 1s does the adjustable parameter k nearly equal these defined quantities. Table I also presents the parameters l and L. Again, only for C 1s do l and L have about the same value, and it is clear that the CNDO correlations using eq 1 do not correspond to the use of the potential except in the case of C 1s. This is not surprising, since even *ab initio* MO wave functions do not give good ΔBE's unless they are in terms of an accurate basis set,[6,10] and one could not expect *a priori* that a minimum basis semiempirical MO scheme would do better.[7,10]

Table I. CNDO Defined Quantities in eV, K_A and L of eq 8, Coulomb Integral k_{AC}, and Least-Squares Parameters k and l of eq 1[a]

	K_A	k_{AC}[b]	k[b]	L[c]	l[d]
C	22.108	22.0	21.9	0.769	0.8
N	26.530	26.4	21.5	0.0	−1.7
O	30.951	30.7	25.8	0.0	−0.4
F	35.373	35.1	27.6	3.248	1.7
S	16.477	16.5	13.8	0.237	

[a] All in electron volts. [b] From ref 3. [c] Calculated by us using eq 7 and data from ref 3. [d] Calculated by us using eq 1 and the data of ref 3. Because of round-off, these l values are the average of a small range of l values found for each atom. For S, however, values ranging from 0.12 to 3.2 were found. There appear to be mistakes somewhere in the S data of ref 3.

Table II. Valence Potentials at the Nuclei and Various ΔBE Calculations, Based on CNDO–MO Theory[a]

	$-\Phi_{val}$	Eq 1[b]	Eq 5[c]	Eq 6[d]	Exptl[b]
CH_4	89.201	−0.1	0.3	0.3	0.0
$^*CH_3CH_2OH$	89.019	−0.0	0.4	0.4	0.2
$^*CH_3COCH_3$	88.706	−0.2	0.7	0.7	0.5
$^*CH_3COH$	88.597	0.5	0.8	0.7	0.6
$^*CH_3COOH$	88.499	0.4	0.9	0.8	0.7
CH_3OH	87.064	2.1	2.3	2.4	1.6
$CH_3{}^*CH_2OH$	86.848	2.3	2.5	2.6	1.6
CS_2	85.215	3.9	4.1	4.0	2.4
$CH_3{}^*COCH_3$	86.010	3.2	3.3	3.4	3.1
$CH_3{}^*CHO$	85.920	3.3	3.4	3.5	3.2
$CH_3{}^*COOH$	84.714	4.5	4.6	4.7	4.7
CO	88.310	0.9	1.1	1.2	5.2
CO_2	82.476	6.8	6.8	6.8	6.8
CF_3H	80.919	8.4	8.3	8.2	8.1
CF_4	78.930	10.4	10.2	10.1	11.1
rms error		1.23	1.218	1.215	
$C_6H_5NH_2$	136.294	−3.8	−3.7	−3.8	−4.4
NH_3	136.339	−3.9	−3.8	−3.8	−4.3
*NNO	132.835	−1.0	−1.7	−1.5	−1.4
N_2	132.650	−1.7	−1.6	−1.6	0.0
$C_6H_5NO_2$	126.410	1.9	2.2	2.1	1.7
N*NO	125.344	2.9	2.8	2.8	2.6
rms error		0.78	0.763	0.760	
CH_3CHO	190.374	−3.7	−3.2	−3.9	−5.5
$CH_3CO{}^*OH$	191.490	−4.5	−3.7	−4.3	−4.9
$CH_3C{}^*OOH$	190.390	−3.4	−3.2	−2.5	−3.1
C_2H_5OH	190.892	−4.1	−3.5	−4.0	−4.5
CH_3OH	190.323	−3.6	−3.2	−3.4	−4.2
CH_3COCH_3	191.152	−4.4	−3.6	−4.6	−4.1
SF_2O	194.340	−6.2	−5.0	−4.6	−3.7
SO_2	192.974	−5.5	−4.4	−4.4	−3.5
H_2O	191.030	−3.9	−3.5	−3.4	−3.4
CO_2	189.341	−2.6	−2.8	−1.2	−2.3
NNO	190.999	−4.0	−3.5	−3.1	−1.9
CO	186.005	−0.7	−1.2	−1.3	−1.0
O_2	185.706	−0.4	−1.1	−1.2	0.0
rms error		1.22	1.095	0.889	
SOF_2	253.237	−1.5	−0.7	−0.9	−0.8
CHF_3	250.859	0.2	0.3	0.2	0.0
SF_6	251.716	0.6	−0.1	0.2	0.2
CF_4	250.019	0.9	0.7	0.7	0.8
rms error		0.84	0.215	0.121	
CS_2	99.099	0.2	0.7	0.0	0.0
H_2S	99.534	−0.1	0.5	0.4	0.4
SO_2	93.127	4.7	4.3	5.2	5.0
SOF_2	90.993	6.6	5.6	6.1	6.4
SF_6	81.736	14.0	11.1	10.7	10.6
rms error		1.55	0.625	0.174	

[a] Φ_{val} in volts; ΔBE in eV. [b] From ref 3. [c] Parameters (a, b) of eq 5: C (0.967, 0.252); N, (0.597, −1.567); O (0.457, −1.101); F, (0.445, 0.317); S (0.601, 0.752). [d] Parameters (a, b, c) of eq 6: C (20.051, 0.858, 1.030); N (17.018, 0.681, −1.609); O (30.678, 1.633, −1.249); F (16.984, 0.566, 1.379); S (−3.150, −0.787, 0.986).

We might inquire whether an accurate description could be found by consideration of families of quite closely related molecules, as Davis, *et al.*, have done.[8] There are a few such groups for O, N, and F in Table II, where for all molecules we summarized our calculated Φ_{val} and the experimental ΔBE's, based on ref 2. The molecules H_2O, CH_3OH, and C_2H_5OH are one set for O 1s, but ΔBE and $\Delta\Phi_{val}$ are not the same. Similarly CH_3CHO and $(CH_3)_2CO$ are not relatively well described. In fact, CNDO seems rather poor for O 1s and has led to an incorrect ordering of the O 1s BE's in acetic acid.[10] But $C_6H_5NH_2$ and NH_3 for N 1s, and CHF_3 and CF_4 for F 1s, are well described. Clearly one needs to examine larger sets of experimental and theoretical values for such families.

Although generally $\Delta BE \neq \Delta\Phi_{val}$, a previously used approach[7,10] might still be useful; the potential is used, but it is adjusted by least-squares parameters a and b in a trial correlation

$$\Delta BE = a\Delta\Phi_{val} + b \qquad (5)$$

This utilizes the same number of adjustable parameters as eq 1, with "ideal" values $a = 1$, $b = 0$. In the results summarized in Table II, eq 5 for C, N, and O gives only slightly smaller rms errors than eq 1, with the rather small sets of F 1s and S 2p ΔBE's being a bit more accurately described. The *formally* more well-grounded approach of eq 5 thus offers little practical improvement over the eq 1 method, and the deficiency of CNDO for these systems is still obvious.

But one further possibility may be considered here. This is noticed if one examines eq 4 and 5; in both equations the *relative* weights of the local charge contribution (K_Aq_A) and the other-atom contribution (V) are fixed. Notice further that in the approach of eq 1, the local charge contribution is adjusted *via* the parameter k, while the other-atom contributions in V always get their full unit weight. Both observations suggest that one might more accurately describe the ΔBE's by letting both the local- and other-atom contributions be adjustable in the form

$$\Delta BE = aq_A + bV + c \qquad (6)$$

Of course q_A and V are not independent variables since the sum of the charges in the system (q_A and all q_B) must equal the net charge (zero for all cases here); but inasmuch as the CNDO theory is approximate and we seek "empirical" relationships, the approach merits examination. (The older atomic-charge-only correlations[2-4] are a special case of eq 6 if $b = 0$ is required.) Fits according to eq 6 are also summarized in Table II, the results being similar to eq 5 applications. Only the calculated F 1s and S 2p ΔBE's are essentially more accurate than before, but these cases fit just four and five pieces of data, respectively, with three adjustable parameters, and we should really look at larger data sets to make proper comparisons.

We conclude with two remarks. First, if CNDO is to be used for ΔBE's, one should focus attention on families of closely related molecules[8] and try the more rigorous potential approaches of eq 4 and 5 or the more flexible adjustment of eq 6. Second, there is a need for more accurate valence electron description by approximate MO schemes and other MO schemes should be considered[10] in connection with ΔBE's.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XV. The Protonation of Benzene

Warren J. Hehre[1a] **and John A. Pople***

Contribution from the Laboratoire de Chimie Théorique,[1b] *Université de Paris-Sud, Centre d'Orsay, 91 Orsay, France, and the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.* *Received January 13, 1972*

Abstract: Simple *ab initio* molecular orbital theory is applied to the study of the possible geometries and energies of protonated benzene. Using the STO-3G minimal basis set the optimum form of the ion is found to be one in which the proton is bonded to a ring carbon which assumes approximately tetrahedral coordination. The form in which the proton bridges a carbon–carbon bond is found to be less favored, and structures corresponding to edge and face protonation are found to be poorer still. The calculated proton affinity of benzene is in good agreement with experiment, and a theoretical value is proposed for the energy required for the proton to migrate from one carbon to another through a bridged intermediate.

In previous papers in this series we have considered the application of *ab initio* molecular orbital theory to the study of the electronic structure of simple organic molecules and ions. We extend our applications now to consider the species $C_6H_7^+$, the ion formed upon the protonation of benzene.[2] This system is interesting and warrants special consideration primarily because it and ions of similar type have long been implicated in processes of electrophilic aromatic substitution. Any structural information derived theoretically on this ion could in principle lead to a more thorough understanding of the possible mechanisms of such reactions. A further motive for this research is to enable us to test whether or not the structure for protonated benzene resembles to any extent the structures of simpler carbocations, in particular the ethyl cation. It is likely that any serious direct attempt to elucidate the transition states involved in aromatic substitution reactions by *ab initio* methods can only be carried out realistically on model systems.

It must be cautioned at the outset that the results of our technique, as well as the majority of others that have been applied to this problem, should really be compared only with experimental measurements performed on the dilute gas. We make no pretense of understanding at this time the effect of solvent media on the structure and energetics of ionic species, and hope only that the model we present might be useful as a starting point for detailed treatments of such effects.

Quantum Mechanical Method

We have applied single-determinant *ab initio* molecular orbital theory throughout. Unless otherwise specified, a minimal basis set of functions closely related to Slater-type orbitals is used. In this basis (STO-3G), each atomic function is replaced by a least-squares-fitted sum of three Gaussian functions. These are associated with the standard molecular set of expo-

---

[1] (a) National Science Foundation Postdoctoral Fellow 1971–1972. (b) The Laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements, associated with the CNRS.

[2] For a recent review see G. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971), or for a more classical treatment, A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 11.