Binding Energy Shifts for Carbon, Nitrogen, Oxygen, and Sulfur Core Electrons from Extended Hückel Theory Valence Molecular Orbital Potentials at the Nuclei

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Abstract: The potential at a nucleus has been calculated as the quantum mechanical average from extended Hückel wave functions for a large number of C, N, O, and S containing molecules. Experimental core level binding energy shifts have been correlated against the calculated potentials. Good fits were found for 1s in C and O, and for 2p in S, while N 1s shifts were poorly described. Discussion of the results and comparison to other approaches and their applicability, as well as suggestions for further experimental and theoretical studies, are given.

Since the demonstrations[2] that shifts in core-electron binding energies (which we denote by ΔBE) are essentially the same as shifts in the quantum mechanical average of the potential at the nucleus on which the core orbital is located, there has been increasing interest in the use of simple electronic structure models to calculate potentials and, hence, the binding energy shifts.[3-5]

In the present paper we extend our previous work[3] in which C 1s ΔBE's were successfully fit to the potential at the nuclei (Φ_{val}), calculated as the quantum mechanical average from extended Hückel theory (EHT) molecular orbital (MO) wave functions for valence electrons. That paper[3] should be consulted for specific remarks about the method, while the general background can be found in ref 2b, 4, and 5. As we have emphasized previously,[3,5] we do not generally expect that $\Delta BE = \Delta\Phi_{\mathrm{val}}$ will be an equality for Φ_{val} from approximate valence MO theories (especially those as crude as EHT). Rather, we hope that Φ_{val} will be a useful parameter against which to correlate measured ΔBE's (and subsequently predict and interpret other ΔBE's). It is certainly more reliable than the simple "atomic charge" of the atom whose core levels are considered,[3,5] and it is much easier to obtain (especially for large molecules) than, say, core orbital energies from *ab initio* all-electron SCF–MO calculations, which in themselves do not give quantitative measures of ΔBE's unless a large, accurate basis set is used.[3,5]

The study here follows the same pattern as before,[3] with the following exceptions. (a) Instead of standard Slater orbital exponents we used the best-atom exponents from atomic calculations of Clementi and Raimondi.[6] H 1s exponents were 1.25. (b) In the Gaussian fits to the Slater-type orbitals,[3] 3G STO fits were used instead of 5G fits. This simplifies the calculation of nuclear attraction integrals needed for Φ_{val}, with no essential change in accuracy, as determined in numerous test calculations by us. (c) Standard molecular geometries[7] were used except where obviously inappropriate, in which case experimental values[8] were used. We also required the additional diagonal matrix elements of −20.08 and −13.32 eV for S 3s and 3p, respectively.[9]

Using a linear least-squares fit of the form

$$\Delta BE = a\Phi_{\mathrm{val}} + b \qquad (1)$$

we examined 1s ΔBE's for C, N, and O; and 2p ΔBE's for S. Note that eq 1 does not explicitly contain $\Delta\Phi_{\mathrm{val}}$ from a reference molecule; the parameter b can absorb that. All discussion is relevant to isolated gaseous molecules, so no experimental or theoretical problems of solid-state effects and work functions need concern us. This will, however, restrict us to a limited set of data.

Results for the four atoms are tabulated in Tables I–IV and plotted in Figures 1–4. References for the experimental ΔBE's are given in footnotes to the tables, while the least-squares parameters a and b of eq 1, along with the root-mean-square errors of the fits, are given in the figure captions. We shall discuss the results atom by atom.

The C 1s BE's studied here are for a larger, more varied set than in our previous study,[3] and this variety shows up in the $\Delta BE - \Phi_{\mathrm{val}}$ fit of Figure 1. However, except for CO, which has generally given trouble before,[3,10] the fit is systematic; systems with C bonded to second row atoms (Cl and S) seem to have their own essentially linear relation and should be treated separately, as we have done in Figure 1 and Table I. Indeed, in future work one might do well to look for correlations within families of similar molecular structure,

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[5] *Cf.* also papers by the authors of ref 3 and 4 in the "Proceedings of the International Conference on Electron Spectroscopy, Asilomar, Calif., Sept 7–10, 1971," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, in press.

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Table I. EHT Calculated Φ_{val} and Least-Squares Fits[a] of ΔBE to Φ_{val} for C 1s Measured from CH_4

		ΔBE, eV	
Molecule	$-\Phi_{val}$, au	This fit	Exptl[b]
CH_4	3.016	−0.2	0.0
C_2H_6	3.009	−0.2	−0.2
C_2H_4	3.028	−0.4	0.1
C_2H_2	3.029	−0.4	0.4
C_6H_6	3.004	−0.1	−0.4
CH_3F	2.733	2.7	2.8
CH_2F_2	2.465	5.6	5.6
CHF_3	2.209	8.2	8.3
CF_4	1.963	10.8	11.0
CH_3OH	2.857	1.4	1.6
$*CH_3CHO$	2.897	1.0	0.6
CH_3*CHO	2.640	3.7	3.2
H_2CO	2.634	3.8	3.2
$*CH_3CH_2OH$	3.002	−0.1	0.2
CH_3*CH_2OH	2.850	1.5	1.6
$*CH_3COOH$	2.896	1.0	0.7
CH_3*COOH	2.547	4.7	4.7
HCOOH	2.534	4.8	5.0
$*CH_3CN$	2.794	2.1	2.9
CH_3*CN	2.707	3.0	2.6
HCN	2.724	2.8	2.6
C_6H_5F:[c] C_α	2.706	3.0	2.3
C_β	2.956	0.4	0.0
C_γ	2.978	0.2	0.0
C_δ	3.000	−0.1	0.0
CO_2	2.409	6.1	6.8
CO	2.905		5.2
CS_2	2.507		2.4
CH_3Cl	2.781		1.6
CH_2Cl_2	2.548		3.1
$CHCl_3$	2.318		4.3
CCl_4	2.093		5.5

[a] The last six molecules were omitted from the least-squares fit. See text and Figure 1 for illumination. [b] See ref 3, 4, 10, 11, and 12 for experimental data. [c] Notation for fluorobenzene:

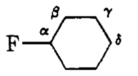

Table II. EHT Calculated Φ_{val} and Least-Squates Fits of ΔBE to Φ_{val} for N 1s Measured from N_2

		ΔBE, eV	
Molecule	$-\Phi_{val}$, au	This fit	Exptl[a]
N_2	4.574	−1.5	0.0
$*NNO$	4.775	−2.4	−1.4
$N*NO$	3.763	2.1	2.6
NO_2	3.876	1.6	2.5
NH_3	4.954	−3.3	−4.3
$C_6H_5NH_2$	4.825	−2.7	−4.4
$C_6H_5NO_2$	3.690	2.5	1.7
CH_3CN	5.193	−4.3	−3.8
NO	4.571	−1.5	0.4

[a] See ref 3, 10, and 12.

Table III. EHT Calculated Φ_{val} and Least-Squares Fits of ΔBE to Φ_{val} for O 1s Measured from O_2

		ΔBE, eV	
Molecule	$-\Phi_{val}$, au	This fit	Exptl[a]
O_2	6.523	−0.1	0.0
NNO	6.902	−2.5	−1.9
NO_2	6.821	−2.0	−1.8
CH_3OH	7.111	−3.8	−4.2
CH_3CHO	7.297	−5.0	−5.5
SO_2	7.131	−3.9	−3.5
H_2O	7.086	−3.6	−3.4
SOF_2	7.254	−4.7	−3.7
CO	6.722	−1.3	−1.0
NO	6.545	−0.2	0.2
CO_2	6.894	−2.4	−2.3
CH_3CH_2OH	7.121	−3.9	−4.5
H_2CO	7.238	−4.6	−5.5
$HC*OOH$	7.268	−4.8	−4.3
$HCO*OH$	6.815	−1.9	−2.7
CH_3C*OOH	7.322	−5.1	−4.9[b]
CH_3CO*OH	6.830	−2.0	−3.1[b]

[a] See ref 10 and 12. [b] The assigned experimental shifts of ref 10 have been switched here, because of (i) analogy with HCOOH, where double ζ calculations[12] indicate a larger shift for the carbonyl O; (ii) explicit *ab initio* calculations by Clark and Lilley[13] on CH_3COOH, which indicate this order; (iii) Jolly's reassignment of the BE's based on his thermodynamic model.[14] The circles on Figure 3 indicate the previous assignment; the triangles, the corrected one.

Table IV. EHT Calculated Φ_{val} and Least-Squares Fits of ΔBE to Φ_{val} for S 2p Measured from H_2S

		ΔBE, eV	
Molecule	$-\Phi_{val}$, au	This fit	Exptl[a]
H_2S	3.838	−0.6	0.0
C_4H_4S	3.658	0.7	−0.4
CS_2	3.805	−0.4	−0.4
SO_2	3.183	4.3	4.6
SOF_2	3.014	5.6	6.0
SF_6	2.381	10.4	10.2

[a] See ref 15.

instead of mixing a wide variety of systems as we have done here. (This proved to be a good procedure in the CNDO work of Davis, *et al.*,[4] on the fluorinated methanes and benzenes.) Presently, however, there is a paucity of data of the sort required for this approach, and, with the above exception, we group all molecules together. Still, the correlation for C 1s is a good one, as the Table I data show, and as in our earlier work it is a bit better than the point-charge potential models from CNDO calculations.[10]

ΔBE's for N 1s are not well described quantitatively by the present calculations. This is not surprising in view of the crude nature of EHT, the rather varied nature of the rather small number of molecules considered, and the relatively anomalous N 1s correlations (compared to other atoms) found previously by other workers (see, *e.g.*, the summary on p 456 of ref 16). It would be desirable to have data for more closely related N-containing molecules to see whether EHT could be useful; we intend to obtain some such experimental data on the Notre Dame ESCA spectrometer. We have made one further attempt to examine the usefulness of the EHT Φ_{val} model for N; the nuclei acid cytosine was studied and compared to the measured and theoretical (*ab initio*) shifts reported by Barber and

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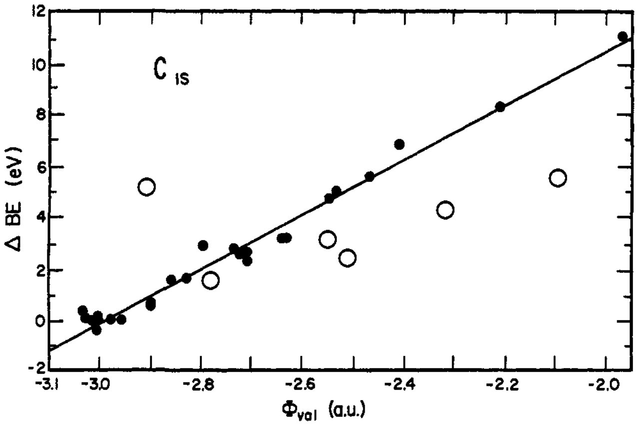

Figure 1. Correlation of C 1s ΔBE's with Φ_{val} from EHT calculations. The circles lying below the line refer to molecules containing second row atoms (*cf.* Table I and the text). The isolated circle above the line is CO. Least-squares parameters: $a = 10.516$, $b = 31.474$, rms error = 0.39.

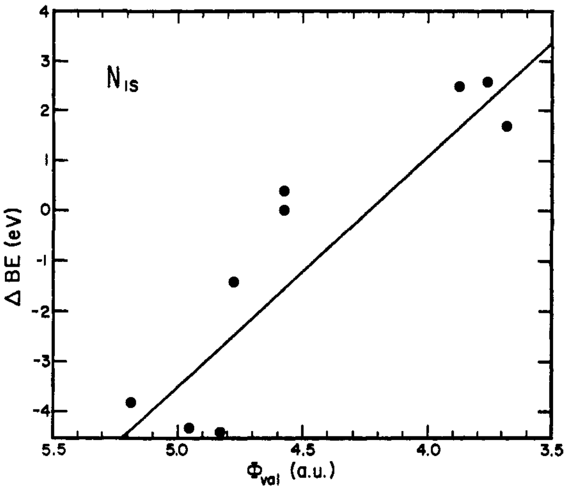

Figure 2. Correlation of N 1s ΔBE's with Φ_{val} from EHT calculations. Least-squares parameters: $a = 4.520$, $b = 19.145$, rms error = 1.11.

Clark.[17] This is an interesting case because the relative N 1s BE's are in an opposite sense to the *ab initio* calculated charges at the N atoms, contrary to the usual BE–charge relation.[10] We found the same to be true for our calculated EHT charges. However, our calculated EHT Φ_{val} of −5.1818, −4.8923, and −4.5672 au for N_3, N_7, and N_1, respectively (notation of ref 17), correlates very well with the relative BE's of 0, 0.9, and 1.8 eV, with a slope slightly different from the Figure 2 fit. We also performed similar EHT studies for the two other nucleic acids, adenine and thymine, and found correct relative ordering of the BE's against Φ_{val}, with considerably less effort than in the *ab initio* studies.[17] Calculated atomic charges were again unreasonable compared to ΔBE's, since atoms with very nearly the same calculated charge have rather different BE's.

O 1s ΔBE's are well described by our EHT calculations, as Table III and Figure 3 show. The fit is a bit better than that from earlier CNDO point-charge potential models[10] and for a larger set of molecules.

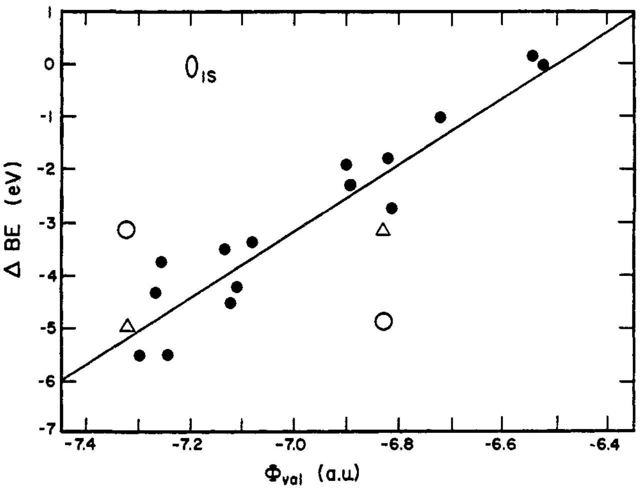

Figure 3. Correlation of O 1s ΔBE's with Φ_{val} from EHT calculations. The two circles refer to the original CH_3COOH assignment of ref 10. The triangles are the reassigned ones (*cf.* text and Table III). Least-squares parameters: $a = 6.377$, $b = 41.525$, rms error = 0.57.

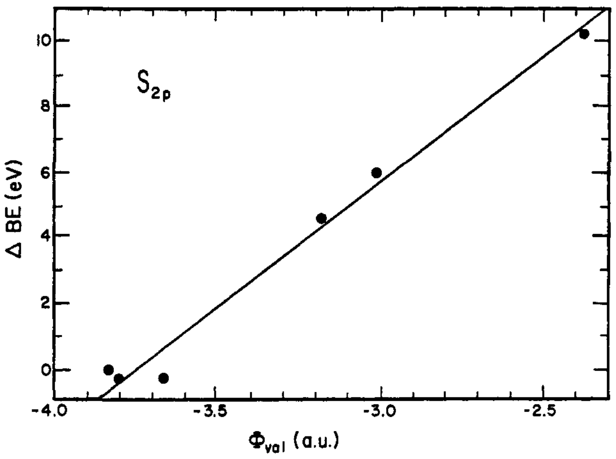

Figure 4. Correlation of S 2p ΔBE's with Φ_{val} from EHT calculations. Least-squares parameters: $a = 7.591$, $b = 28.485$, rms error = 0.57.

Table III and Figure 3 also illustrate how a misassigned spectrum can be corrected (or an unassigned one assigned) if a good correlation is found. We had thought because of the otherwise excellent correlation that the O 1s BE assignments[10] in CH_3COOH should be switched. *Ab initio* $\Delta(-\epsilon)$ calculations by others[13] confirmed the reassignment, as did Jolly's thermodynamic model.[14]

As with N 1s, there are only a few S 2p ΔBE's known (recall, only gas-phase results are considered), but as Table IV and Figure 4 show, the EHT Φ_{val} correlation for S 2p is an excellent one. Indeed, the "predicted" ΔBE's are as good as the *ab initio* ones[15] and better than those from the CNDO point-charge potential model.[10]

To summarize, we have found good correlations of core ΔBE's and Φ_{val} from EHT for C, O, and S atoms and a poorer correlation for N atoms. We hope these correlations and the general approach will be useful to other workers in core-electron studies and that further experimental measurements of the sort previously sug-

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[17] M. Barber and D. T. Clark, *Chem. Commun.*, 23, 24 (1970).

gested will be done. Of course, EHT is a very crude MO theory, and we would further suggest that other more accurate MO schemes be investigated. Some such work has recently appeared for the CNDO model,[4] and in a separate paper we shall discuss our own CNDO studies.[5]

Pulse Radiolysis Study of Succinonitrile in the Rotator Phase[1,2]

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Abstract: A transient absorption spectrum ($t_{1/2} = 0.23$ μsec) has been detected in the pulse radiolysis of succinonitrile, a plastic crystal at room temperature. This absorption is not produced in the presence of 1 mol % tetracyanoethylene (TCNE) and the spectrum of TCNE$\cdot^-$ is observed instead. The value of λ_{max} (450 nm) for the transient corresponds to the absorption maxima observed in the low-temperature spectra of monomer radical anions from acetonitrile and adiponitrile. On the basis of these results, the transient spectrum is assigned to a monomer radical anion of succinonitrile although the possibility of a dimer species similar to that observed at low temperature cannot be excluded. The first-order decay of the radical anion is attributed to the unimolecular dissociation to $\cdot CH_2CH_2CN$ and CN^-. In addition to the radical anion, a long-lived species is produced which absorbs most strongly in the ultraviolet.

In the pulse radiolysis of organic liquids, studies of transient ions by optical absorption spectroscopy have been largely restricted to solvated electrons and to ions produced by reactions with suitable charge scavengers.[4] The detection of these ions is facilitated by a $G\,\epsilon_{max}$ product which frequently exceeds 1×10^4, where G is the 100-eV yield of species with lifetimes exceeding the resolution time of the equipment and ϵ_{max} is the extinction coefficient in M^{-1} cm^{-1} at the absorption maximum (λ_{max}). Two pulse radiolysis studies of acetonitrile solutions containing aromatic hydrocarbons such as biphenyl[5] and anthracene[6] have been reported in which transient absorption spectra were readily observed and identified as belonging to the radical anion and triplet state of the solute. For pure acetonitrile, however, there is only a brief report[5] of a short-lived transient ($t_{1/2} < 5$ μsec) with a very weak absorption at 660 nm which was tentatively attributed to a solvated electron. Even this observation is in doubt because in a later study of the pulse radiolysis of oxygen-free acetonitrile,[6] no absorption could be detected between 280 and 800 nm despite high sensitivity and a resolution time of 100 nsec.

By contrast, esr and optical studies of γ-irradiated acetonitrile in the solid state at low temperature have definitely shown that the dimer and monomer radical anions of acetonitrile are produced and stabilized in crystal I and crystal II, respectively.[7] The optical absorption spectrum of the dimer radical anion in a polycrystalline sample has two bands with λ_{max} at 510[8,9] and 310 nm,[9] whereas the corresponding spectrum of the monomer radical anion has only one clearly defined band with λ_{max} at 430 nm.[9] In similar low-temperature irradiation studies, the dimer radical anion of succinonitrile was identified in both crystalline phases.[10] Its powder esr spectrum is identical with that of the acetonitrile dimer radical anion[11] and λ_{max} for the optical absorption is located at 540 nm.[10]

Succinonitrile differs from other simple organic cyanides in having a relatively high melting point (331°K). Also, the solid phase above 233°K (crystal I) is a transparent plastic crystal in which the rotational motion of the individual molecules is more characteristic of a liquid than of a solid.[12] It was thought that the physical properties of this plastic crystal[13] which are intermediate between those of a liquid and a solid might favor the detection by pulse radiolysis of a succinonitrile radical anion (or solvated electron) at room temperature. This finding would be of particular interest in view of the close resemblance between the γ-irradiation results for acetonitrile and succinonitrile at low temper-

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(2) This research was supported by the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory operated under contract with the Union Carbide Co. and at The University of Tennessee under Contract No. AT-(40-1)-2968; this is AEC Document No. ORO-2968-71.

(3) (a) The University of Tennessee; (b) undergraduate on leave from New College, Sarasota, Fla. 33578; (c) Oak Ridge National Laboratory.

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