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Author
Davis, D.W.

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D. W. Davis and D. A. Shirley

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A RELAXATION CORRECTION TO CORE-LEVEL BINDING ENERGY

SHIFTS IN SMALL MOLECULES[†]

D. W. Davis and D. A. Shirley

Department of Chemistry
and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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A theoretical method for correcting core-level binding-energy shifts for final-state relaxation effects in the framework of the CNDO model is derived and compared to measured shifts of carbon, nitrogen, and oxygen 1s electron binding energies in gaseous molecules.

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Core-level binding-energy shifts in molecules are given by energy differences between initial and final states in photoemission processes, although they are usually interpreted in terms of initial-state properties alone. This approach would yield correct shifts if the passive molecular orbitals remained "frozen" during photoemission, or if they relaxed by the same amount (in total energy) for all molecules. Differential relaxation from one molecule to the next will alter the shifts. It is therefore useful to correct for this effect. In this Letter a simple relaxation correction, applicable to "potential energy" models of binding-energy shifts, is derived and applied to fifty-four cases.

Basch[1] and Schwartz[2] have shown independently that differences in orbital energies of 1s electrons from one environment to another are quite

accurately equal to the corresponding differences in potential energy of the

1s electrons in their initial states,

$$\Delta \in (1s) \quad = \quad \Delta V(1s) \quad . \tag{1}$$

Since measured shifts in 1s binding energies have been found to agree

rather well with orbital energy differences as obtained from ab initio

molecular-orbital calculations on initial states[3-6], it follows that binding-

energy shifts can be predicted from shifts in the potential energies of the

1s orbitals;

$$\Delta E_B(1s) \quad = \quad - \Delta V(1s) \quad . \tag{2}$$

Within the framework of ab initio calculations above, this result is not

very useful for estimating binding-energy shifts, because the orbital energies

yielded by ab initio calculations could as well be used directly. Less

sophisticated molecular-orbital calculations do not yield 1s orbital energies,

however, and eq. (2) can be used to good advantage for predicting binding-

energy shifts in conjunction with such calculations.

Recently CNDO theory[7] has been used[5,6] to fit 1s binding-energy

shifts in series of molecules containing first-row elements. For each element

the external potential energy, $V_e^{(i)}$, and the charge q_i on the host atom

were calculated. Measured binding-energy shifts were then fitted to a two-

parameter equation of the form

$$E_B^{(i)} \quad = \quad kq_i + V_e^{(i)} + \ell \quad , \tag{3}$$

to obtain empirical values of k and ℓ.

Recently Davis et al.[8,9] have found that shifts in C 1s and F 1s

binding energies can be predicted in CNDO theory by a simple calculation on

the initial state, without the necessity of adjusting parameters. They

evaluated r^{-1} integrals for both the host atom and other centers directly.

Very good agreement with experiment was found within a series of similar

compounds, with poorer agreement from one such series to another.

The above estimates of binding-energy shifts were all based on initial

states only. While the presently available agreement with experiment to

within 1-2 eV or better in most cases is gratifying, a point must be reached

in this approach beyond which further refinements based on initial states

alone are futile, because part of the essential physics of the ionization

process --- namely, relaxation in the final state --- has been entirely

neglected. It has been shown that ab initio 1s hole-state calculations can

be done directly on molecules[10], and explicit relations describing relaxation

in the final state have also been given[11]. Hedin and Johansson[11] derived an

expression for the binding energy of a core orbital. In our notation their

result is

$$- E_B(1s) \cong \in(1s) + 1/2 \langle 1s|V_R|1s \rangle \quad . \tag{4}$$

Here V_R is a relaxation potential energy arising from the difference between

the Hartree-Fock potential V_k of the passive orbitals in the final (1s-hole)

state and the initial state. Specifically,

$$V_R = \sum_{k \neq 1s} \left(V_k^{(f)} - V_k^{(i)} \right) \quad . \tag{5}$$

Hedin and Johansson rearranged eq. (4) to prove a result that Liberman[12]

had discovered earlier,

$$- E_B(1s) = \frac{1}{2} [\in(1s) + \in(1s)^*] \quad , \tag{6}$$

where $\in(1s)^*$ is the orbital energy of a 1s electron in the hole state. Let us write each orbital energy as the sum of the interaction energy of the 1s electron with its own nucleus, plus a "potential-energy" term that includes interactions of the 1s electron with other electrons and other nuclei,

$$\in(1s) = \langle 1s|h|1s \rangle + \langle 1s|V|1s \rangle . \qquad (7)$$

Combining eq. (6) and (7), taking differences (as between two compounds), and noting that the differences in the first terms of eq. (7) are negligibly small[2], we have

$$\Delta E_B(1s) \cong -\frac{1}{2} \Delta \langle 1s|(V + V^*)|1s \rangle . \qquad (8)$$

From the work of Basch[1] and Schwartz[2] it is clear not only that to a good approximation the right hand side of eq. (8) can be replaced by the difference in the potential energy of the 1s electron from one molecule to another (neglecting differences in exchange integrals), but also that it is sufficient to evaluate the electrostatic potential ϕ at the host nucleus. Thus for shifts in carbon 1s binding energies,

$$\Delta E_B(C1s) = \frac{e}{2} \Delta[\phi(C) + \phi(C^*)] , \qquad (9)$$

where the relation $e\phi = -V$, appropriate for an electron, has been used, and the asterisk denotes a hole in the carbon 1s shell. The relaxation correction is of course contained in the second potential term, $\phi(C^*)$. If this term were equal to $\phi(C)$, eq. (9) would be essentially equivalent to eq. (2).

In CNDO theory there is no way to calculate $\phi(C^*)$ directly, because this theory does not include 1s orbitals in second-row elements, let alone provide for calculations on states in which these orbitals are only singly occupied. It is possible, using CNDO theory, to estimate shifts in $\phi(C^*)$,

however. We may invoke the idea of "equivalent cores".[13] Since 1s electrons shield out essentially one complete nuclear charge, the attraction exerted on valence orbitals by the "core" consisting of a nitrogen nucleus plus a doubly-occupied 1s shell is essentially equal to that exerted by a carbon nucleus plus a singly-occupied 1s shell. For purposes of estimating shifts in the potential at the nucleus arising from "relaxed" valence orbitals we may there-fore simply substitute $\phi(N)$ for $\phi(C^*)$ in eq. (9), obtaining

$$\Delta E_B(C1s) = \frac{e}{2} \Delta[\phi(C) + \phi(N)] \quad . \qquad (10)$$

Since photoemission is a very fast process, the same initial-state molecular geometry is used to calculate $\phi(N)$ and $\phi(C)$, i.e., valence electrons have time to relax, but nuclei do not. We may therefore obtain an estimate of $\Delta E_B(C1s)$ by carrying out two CNDO calculations for each molecule, one on the ground state and one on an isoelectronic state with the same molecular geometry but with nitrogen substituted for carbon.

By using this approach we have estimated thirty-five carbon 1s, nine nitrogen 1s, and ten oxygen 1s shifts in a number of small molecules containing up to twelve atoms. The results are compared with experiment in Figs. 1-3. Experimental values were taken from several sources[4,5,6,8,9,14-16]. Only gas-phase shifts were used.

The carbon results show very good agreement between experiment and theory both with and without the relaxation correction, especially considering that these calculations predict shifts, rather than just fitting them. The standard deviation from a least-squares fitted line of unit slope is slightly smaller for the relaxation-corrected case (0.84 eV vs 1.06 eN, table 1). In particular the result for CO is greatly improved by this correction. We may

therefore make the preliminary observation that the relaxation correction

brings the CNDO potential model into better agreement with experiment, if a

wide variety of molecules is considered. Inspection of Fig. 1 shows systematic

discrepancies between the relaxation-corrected theory and experiment, however.

There is a general tendency for shifts to be exaggerated. This appears both

as a slope of slightly more than unity in the ratio $\Delta E_B(\text{theo.})/\Delta E_B(\text{expt.})$,

and - more dramatically - as large excursions in the theoretical shifts of

the highly - oxidized carbons in CO_2 and CF_4. Another effect is also present.

The agreement between experiment and theory within a series of similar compounds

is much better than that over a wide range of compounds. This effect is still

under study, and we shall simply note here that if only alkanes and fluoro-

alkanes are considered, a standard deviation of only ~ 0.4 eV is obtained

between experiment and theory (table 1), based on the fifteen measured shifts

available.

In nitrogen compounds the agreement of theory with experiment is

dramatically improved by the relaxation correction, with the standard deviation

falling from 2.3 eV to 1.3 eV. Without this correction the agreement is so

poor as to obviate the use of the CNDO potential model. With it the theoretical

predictions are quite good.

The oxygen shifts are not improved by the relaxation correction. For

molecular oxygen itself we have been unable to obtain a reasonable description

of FO^+ in the CNDO model. The nine other available shifts give a standard

deviation of 1.15 eV with the relaxation correction versus 0.84 eV without it

(table 1).

To be theoretically acceptable, this method for correcting binding

energies must not only give improved values of binding-energy shifts (as in

eq. (1)), but the relaxation correction to E_B itself should also be approximately of the right magnitude. By arguments similar to those yielding eq. (10), we have derived from eq. (4) the relation

$$- E_B(\text{C1s}) \cong \in(\text{C1s}) + \frac{e}{2}[\phi(C) - \phi(N)] \qquad (11)$$

for carbon 1s shifts, and similar relations for shifts in other elements. The second term on the right is the relaxation energy, V_R. In table 2 values of V_R obtained from the model presented here are compared with differences between ab initio hole-state and orbital-energy results for several molecules. The good agreement both supports the validity of this approach and indicates its possible usefulness in estimating binding energies from orbital energies.

Finally, some physical insight into the origins of differential molecular relaxation can be obtained by studying the charges assigned the host atom in the CNDO scheme before and after photoemission. Table 3 gives the initial charge q and the changes Δq for selected carbon cases from fig. 1 plus all the nitrogen and oxygen shifts shown in figs. 2 and 3: Let us consider the carbon charges. When a C 1s electron is ejected, the remaining electronic charge in the molecule collapses toward the positive hole to minimize the total energy (only very fast ($<10^{-15}$ sec) adiabatic processes are of interest here, because these processes alone shift the full-energy photoelectron lines). In methane and the fluoromethanes this leads to essentially complete charge compensation: in fact the valence electron "population" assigned to the carbon atom in the hole-state ion is actually slightly larger than in the molecular initial state. That a large fraction of this compensation should occur in these molecules is not surprising, because there are four single bonds from which the positive hole can draw electrons without creating strong centers of

positive charge elsewhere. By contrast, a very different situation obtains

in the multiple-bonded small molecules CO, HCN, and CO_2. In the extreme case

of CO, for example, the valence shell population assigned to carbon in the

hole state is only about 0.5 larger than in the initial state. Further

electronic charge could only come from the single oxygen atom, and this would

require too much charge separation. Thus the relaxation energy of CO is

expected to be smaller than that of methane.

In summary, the relaxation correction given here appears to give

improvement over the already reasonably good agreement between theoretical

and experimental shifts that can be obtained with the CNDO potential model.

Table 2 shows that V_R is quite accurately equal to the actual relaxation energy,

so this correction could be useful in estimating binding energies from orbital

energies. The predictive value of this model can be enhanced by taking a

more empirical approach. The slope, k, in eq. (3) could be adjusted, and/or

only series of similar molecules could be considered. Further work along

these lines is underway.

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Table 1. Quality of theoretical fits to 1s binding energies.

Case	Intercept (eV)[a]		Standard Deviation (eV)	
	CNDO potential Model Only	Relaxation Correction Added	CNDO Potential Model Only	Relaxation Correction Added
Thirty-five C 1s shifts	0.22	-0.18	1.06	0.84
Fifteen C 1s shifts in fluoroalkanes	0.59	0.19	0.35	0.41
Nine N 1s shifts	1.16	1.18	2.35	1.30
Ten O 1s shifts	2.12	0.70	0.84	1.15

[a] All shifts are referred to the hydrides CH_4, NH_3, and H_2O. A straight line of unit slope was fitted to the data, as in figs. 1-3. This intercept is the theoretical value of the line at an experimental shift of zero.

Table 2. Comparison of V_R with _ab initio_ results (energies in eV)

Molecule	$-\epsilon(1s)$	E_B [a]	$-\epsilon_B - E_B$	V_R(this work)
CH_4	305.2[b,c]	291.0[d]	14.2	
			14.4[e]	15.9
$CO(C1s)$	310.7[b]		12.3[e]	11.9
$CO(O1s)$	563.5[b]		21.4[e]	21.5
NH_3	423.5[c]	405.7[d]	17.8	19.0
H_2O	560.1[c]	539.4[d]	20.7	
			20.2[e]	20.6

[a] From hole-state calculations.

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[e] Obtained from a configuration interaction calculation by Hillier et al., (footnote b).

Table 3.

Molecule	q	Δq	V_R	$\Delta E_B{}^a$	$\Delta E_B(R)^a$	$\Delta E_B(\text{Expt})^a$	Ref.
CARBON 1s SHIFTS							
CH_4	-.05	-.04	15.89	--	--	--	-
CH_3F	+.18	-.08	15.92	2.99	2.96	2.80	4
CH_2F_2	+.40	-.10	15.73	5.82	5.98	5.55	8
CHF_3	+.61	-.10	15.38	8.54	9.05	8.30	4
CF_4	+.81	-.08	14.91	11.13	12.11	11.00	4
HCN	+.03	+.18	14.40	.31	1.80	2.60	4
CO	+.04	+.54	12.41	.67	4.65	5.40	4
CO_2	+.54	+.16	12.86	6.57	9.60	6.84	4
NITROGEN 1s SHIFTS							
N_2	0.0	+.38	16.67	2.32	4.66	4.35	4
NO	0.0	0.0	15.73	3.11	6.39	5.15	16
NO_2	.39	-.08	20.39	9.96	8.58	7.35	16
CH_3NO_2	.50	-.02	20.00	11.32	10.33	6.58	15
HCN	-.10	+.41	18.50	1.07	1.59	1.25	4
NH_2NH_2	-.13	+.10	19.98	1.08	.12	.50	14
CH_3NH_2	-.19	+.14	19.75	.37	-.38	-.45	14
NF_3	.36	+.08	19.32	10.20	9.89	8.85	14
ONF_3	.70	-.12	20.63	16.08	14.47	11.45	14
OXYGEN 1s SHIFTS							
CO	-.04	+.29	21.46	4.83	4.00	2.94	4
NO	0.0	+.38	20.35	6.28	6.56	4.14	16
CO_2	-.27	+.38	22.01	2.96	1.58	1.44	4
NO_2	-.20	+.45	20.35	3.93	4.21	2.41	16
CH_3NO_2	-.33	+.36	23.14	.89	-1.62	-.51	15

Table 3. (continued)

Molecule	q	Δq	V_R	ΔE_B^a	$\Delta E_B(R)^a$	$\Delta E_B(\text{Expt})$	Ref.
$HC\!\!\diagdown\!\!_{O*H}^{\diagup O}$	-.24	+.31	22.36	4.06	2.33	.67	4
$HC\!\!\diagdown\!\!_{OH}^{\diagup O*}$	-.30	+.30	23.30	.84	-1.83	-.95	4
NNO	-.28	+.43	22.02	2.53	1.09	1.54	4
CH_3OH	-.25	+.30	22.18	2.25	.70	-.80	4
C_2H_4O	-.21	+.32	22.82	2.43	-.24	-1.05	4

a) All shifts referred to the hydrides CH_4, NH_3, and H_2O.

Figure Captions

Fig. 1. Carbon 1s binding-energy shifts, theoretical vs. experimental,

for a series of gaseous molecules. Filled circles, which go with

lower ordinate scale, represent initial-state CNDO potential-model

calculations. Open circles, and upper ordinate scale, include relaxation

correction. Scales refer to a methane standard. Lines represent best

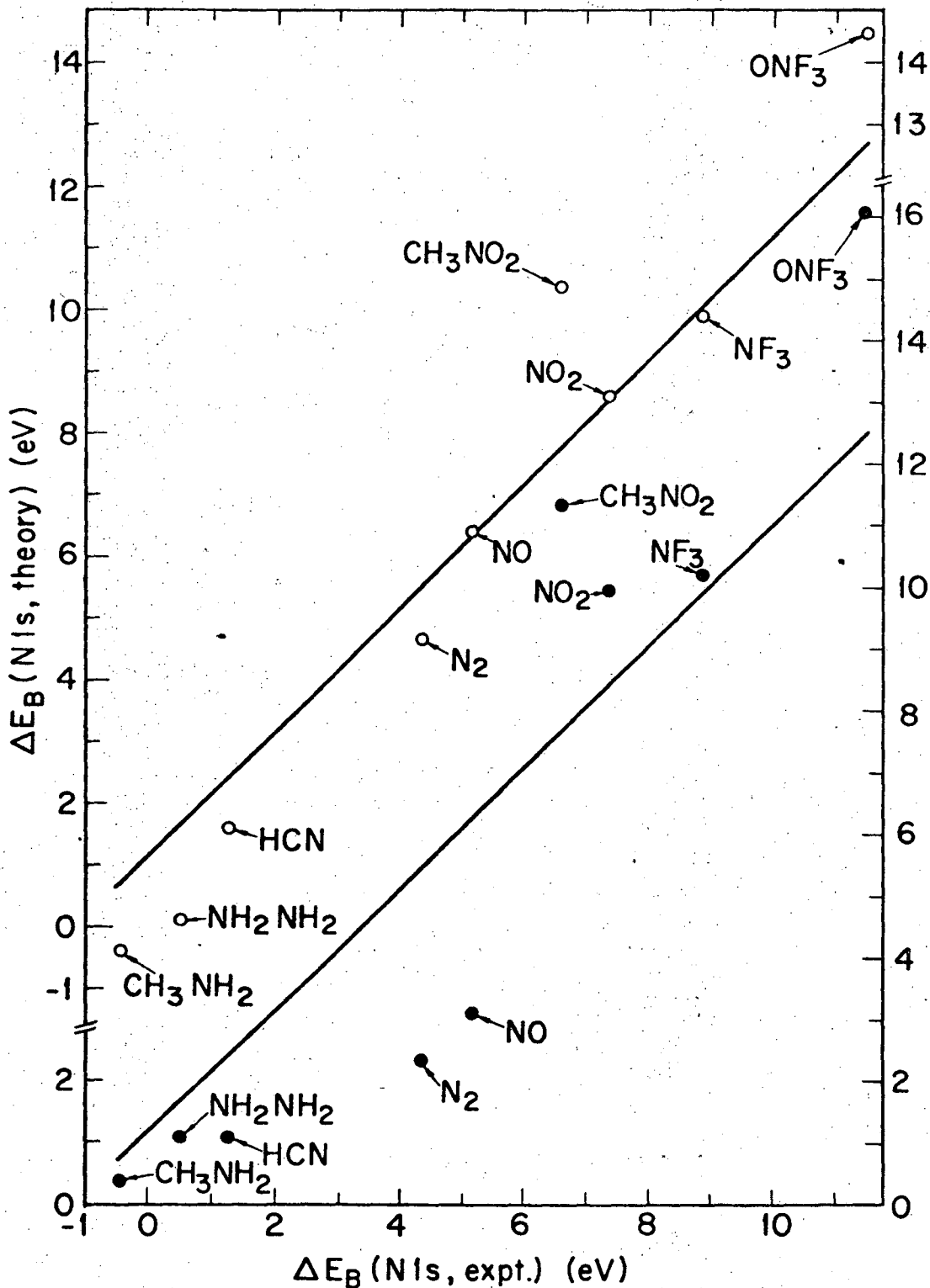least-squares fits under the constraint of unit slope. Selected molecules

are labeled.

Fig. 2. Nitrogen 1s binding-energy shifts for a series of gaseous molecules,

using NH_3 as reference. Format is the same as in Fig. 1.

Fig. 3. Oxygen 1s binding-energy shifts for a series of gaseous molecules,

using H_2O as reference. Format is the same as in Fig. 1.

Fig. 1

Fig. 2

XBL 723-2628

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Fig. 3