An MO Interpretation of the Chemical Shifts of Inner-shell Electrons

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A correlation formula between the chemical shifts of inner-shell electrons and molecular-charge distributions is derived by an MO scheme with CNDO-type approximations. Errors imposed in these schemes are discussed. Reorganization energy terms are briefly discussed in the same level of approximations.

The chemical shifts of inner-shell electrons have been studied in a wide variety of organic and inorganic compounds.[1,2] One interesting feature of the problem is that the chemical shifts change linearly with the charges on the atoms considered. These charges have been estimated by several methods-i.e., methods with using the oxidation number and Pauling's electronegativity differences,[1,3] an iterative extended Hückel method,[4] CNDO method,[5] and several types of non-empirical calculations.[6-11]

In this report, an MO interpretation of the correlation between the chemical shifts of the binding energies of inner-shell electrons in certain molecules and the atomic charges is given by introducing some approximations, and the limitations of these relations are briefly discussed.

Theoretical

By Roothaan's SCF treatment for closed-shell systems, the orbital energy of ith MO, ε_i, is given by:

$$\varepsilon_i = F_{ii} = \sum_{r,t} C_r{}^i C_t{}^i F_{rt} \tag{1}$$

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3) R. G. Albridge, U. Erickson, J. Hedman, C. Nardling, and K. Siebahn, Ark. Kemi, 28, 257 (1968).

4) M. Pelavin, D. Hendrickson, J. M. Hollander, and W. L. Jolly, J. Phys. Chem., 74, 1116 (1970).

5) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, J. Chem. Phys., 49, 3315 (1968).

6) R. Manne, ibid., 46, 4645 (1967).

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8) H. Basch, and L. C. Snyder, Chem. Phys. Lett., 3, 333 (1969).

9) M. E. Schwartz, C. A. Coulson, and S. D. Allen, J. Amer. Chem. Soc., 92, 447 (1970).

10) M. E. Schwartz, Chem. Phys. Lett., 5, 50 (1970).

11) C. A. Coulson, and F. A. Gianturco, Mol. Phys., 18, 607 (1970).

Where $C_r{}^i$ and F_{rs} are the rth AO coefficient of the ith MO and the F_{rs}-element of the Fock operator respectively.

Suppose that the ith MO is mainly constructed by inner-shell AO's; the following derivation can then be easily carried out with considerable accuracy, since the diagonal elements of the Fock operator for inner-shell AO's, F_{ss}, is very large compared with that of the off-diagonal ones F_{rs}:[12,13]

$$\varepsilon_i \simeq \varepsilon_s = F_{ss}, \qquad C_s{}^i \simeq 1.0, \qquad (2)$$

$$F_{ss} = \left(s\left|-\frac{1}{2}\varDelta - \frac{Z_A}{r_A}\right|s\right) + \left(s\left|-\sum_{B\neq A}\frac{Z_B}{r_B}\right|s\right)$$

$$+ \sum_{r,t} P_{rt}\left\{(ss/rt) - \frac{1}{2}(sr/st)\right\}. \qquad (3)$$

In Eq. (3), the first term is the self-core integral, while the second is the nuclear attraction by the other nuclei and the third consists of electronic repulsions. Throughout this report, r, s, t, and u denote atomic orbitals; especially, s denotes the inner-shell AO in question belonging to the A atom. The i and j notations represent occupied MO's, and k and l, vacant ones. The P_{rt} notation is the bond order between r and t AO's.

To connect the orbital energies with the atomic charges, we use the following approximation, using the same notations as in Refs. 14 and 17:

(A), The self-core integral:

$$\left(s\left|-\frac{1}{2}\varDelta - \frac{Z_A}{r_A}\right|s\right) = -I_s - (N_s - 1)(ss/ss)$$

$$- \sum_r^{\text{on A}} N_r\left\{(ss/rr) - \frac{1}{2}(rs/rs)\right\} \qquad (4)$$

and the nuclear attraction:

$$\left(s\left|-\frac{Z_B}{r_B}\right|s\right) = -Z_B(ss/ns_B ns_B) = -Z_B\gamma_{AB}. \qquad (5)^{15)}$$

The above formulae have already been given in a previous paper.[14] (B), The electronic repulsion integrals can be estimated by a CNDO-type approximation[17]:

Thus, Eq. (3) can be re-written as:

$$F_{ss} = -I_s + (P_{AA} - Z_A{}^v)\gamma_{AA} + \sum_{A\neq B}(P_{BB} - Z_B{}^v)\gamma_{AB}, \qquad (6)$$

where the average Coulomb integrals are:

$$\gamma_{AA} = (ss/ns_A ns_A), \qquad \gamma_{AB} = (ss/ns_B ns_B), \qquad (7)$$

and where $Z_A{}^v$ denotes the number of valence electrons on the A atom and ns_A denotes valence s-type AO on the A atom.

When a Mulliken approximation with in Eq. (7) is used instead of the above CNDO-type one, and only the term of S(overlap) is considered, an expression similar to that in Eq. (6) is obtained, but in this case the P_{AA}'s in Eq. (6) become atomic populations.

From Eq. (6), the following simplified relation can be obtained by denoting $(P_{AA} - Z_A{}^v) = -Q_A$ (Q_A is the net charge of atom A):

$$\varDelta\varepsilon_s = \varepsilon_s + I_s = -Q_A\gamma_{AA} - \sum_{B\neq A}Q_B\gamma_{AB}. \qquad (8)^{18)}$$

That is, the shift of the inner-shell binding energy from the atomic ionization energy in certain valence state is correlated with the molecular-charge distribution. The shift of the $\varDelta\varepsilon_s$ for the A atom in different chemical environments, which are denoted as X and Y, is:

$$\delta\varDelta\varepsilon_s(X, Y) = \{Q_A(X) - Q_A(Y)\}\gamma_{AA}$$

$$- \sum_{B\neq A}^{\text{in Y}}Q_B(Y)\gamma_{AB}(Y) + \sum_{B\neq A}^{\text{in X}}Q_B(X)\gamma_{AB}(X). \qquad (9)$$

Eq. (9) indicates that the chemical shifts depend not only on the atomic-charge differences of the A atom in different molecules, but also on the sum of the charges over the other parts of the molecules, since the γ_{AB}/γ_{AA} ratio is not negligibly small. For diatomic molecules of the first-row elements, AB and A_2, $\delta\varDelta\varepsilon_s$-$(AB, A_2) = 0.5$, if $Q_A(AB) = -Q_B(AB) = 1.0$, $\gamma_{AA}(AB) = 1.0$, and $\gamma_{AB}(AB) = 0.5$ (in a.u.).[20] The change in the inner-shell binding energy between the molecules is about 14 eV per unit charge. This is in agreement with the previous results.[19]

Results and Discussion

Tables 1 and 2 summarize the values of some atomic integrals involving the $1S_C$ AO of formaldehyde (in a.u.). By means of these tables we can examine the approximations Eq. (5), and (B). Minimal Slater bases with Slater-rule exponents, except for that of 1.2 for hydrogen, are used throughout the calculations in the present paper. The integrals are evaluated by means of the 4-term Gaussian expansion method.[20]

As shown in Table 1, the approximation introduced

TABLE 1. COMPARISON OF THE NUCLEAR ATTRACTION INTEGRALS $(S_A|(Z_B/r_B)|S_A)$ WITH $Z_B\gamma_{AB}$ IN FORMALDEHYDE (in a.u.)

S_A	B	$(S_A|(Z_B/r_B)|S_A)$	$Z_B\gamma_{AB}$
$1S_C$	O	2.6240	2.6160
$1S_C$	H	0.4855	0.4727
$1S_O$	C	1.7493	1.7089
$1S_O$	H	0.2655	0.2654

12) e.g., W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).

13) E. Clementi, *Chem. Rev.*, **68**, 341 (1968).

14) T. Yonezawa, H. Kato, and K. Yamaguchi, This Bulletin, **40**, 536 (1967).

15) While this work, was in progress, the same relation was pointed out in Ref. 16.

16) See Ref. 22.

17) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

18) A similar equation, obtained by means of an electrostaic model, is given in Ref. 19; that is, $\delta\varDelta\varepsilon_s(XY) = kQ_s + \sum_{j\neq i}\frac{Q_j}{R_{ij}} + l_y$ but here K, which corresponds γ_{AA} in Eq. (8), is taken to be an empirical parameter. The constant, l_y, is determined by means of the reference compound.

19) U. Gelius, B. Roos, and K. Siegbahn, *Chem. Phys. Lett.*, **4**, 471 (1970).

20) As to the integral values, refer to those in Table 2 and also those in Ref. 12.

20) H. Taketa, S. Huzinaga, and K. O-ohata, *J. Phys. Soc. Japan*, **21**, 2323 (1966); S. Huzinaga, *Suppl. Progr. Theor. Phys.*, No. **40**, 52 (1967). R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

TABLE 2. SOME ELECTRON REPULSION INTEGRALS
INCLUDING CARBON $1S$ ORBITALS OF
FORMALDEHYDE (in a.u.)[a]

Type		Type	
$(1S_C1S_C/2S_C2S_C)$	0.8073	$(1S_C1S_C/1S_O1S_O)$	0.4373
$(1S_C1S_C/2P_{xC}2P_{xC})$	0.8072	$(1S_C1S_C/2P_{zO}2P_{zO})$	−0.2452
$(1S_C1S_C/2S_O2S_O)$	0.4360	$(1S_C1S_C/2S_O2P_{zO})$	−0.1190
$(1S_C1S_C/2P_{xO}2P_{xO})$	0.4132	$(1S_C1S_C/2S_C2P_{zO})$	−0.2582
$(1S_C1S_C/2P_{zO}2P_{zO})$	0.4817	$(1S_C2S_C/2S_C2S_C)$	0.0812

a) The z axis is taken to be paralled with the C–O bond.

in Eq. (5) is good. Table 2 indicates that the "average Coulomb" approximation is excellent for one-center integrals and is only correct to within about a 10% error for two-center ones. The two-center Coulomb and hybrid integrels, $(1s_A1s_A/2s_B2p_B)$ and $(1s_A1s_A/2s_A2p_B)$ types, however, are not negligible; therefore, the (B) approximation, i.e., the CNDO-type integal which neglects the above type of integrals, may be

TABLE 3. CALCULATED SHIFTS FOR CARBON $1S$ ELECTRONS

Compounds	E_{obsd} [a]	Q_A [b]	$\delta\Delta\varepsilon$ [c]
C_2H_2	291.2	−0.064	−0.90
C_2H_4	290.7	−0.33	−0.41
C_2H_6	290.6	−0.006	−0.07
CH_3OH	292.7	+0.129	1.40
CO_2	297.64	+0.536	5.45
HCO_2H	295.79	+0.381	3.40

a) Observed binding energies (in eV), T. D. Yhomas, J. Chem. Phys., 52, 1373 (1970); D. W. Davis, J. M. Hollander, and D. A. Shirley, and T. D. Thosmas, ibid., 52, 3295 (1970).
b) Calculated net charges on carbon atom by CNDO/2 method.
c) Calculated by Eq. (9) with CNDO/2 net charges (in eV).

TABLE 4. CALCULATED SHIFTS FOR NITROGEN $1S$
ELECTRONS

Compounds	E_{obsd} [a]	Q_A [b]	$\delta\Delta\varepsilon$ [c,e]	
N_2	402.45	0.0	0.0	
NH_3	398.1	−0.234	−2.96	(−5.92)
$(CONH_2)_2$	400.0	−0.238	−1.73	
$(CH_3)_3NO$	402.2	+0.157	2.09	
C_5H_5N(pyridine)	398.0	−0.142	−2.04	(−6.27)
C_6H_5CN	398.4	−0.165	−2.99	
$NaNO_3$ [d]	407.4	+0.636	−2.59	
$NaNO_2$ [d]	404.1	+0.083	−10.36	
NaN_3 [d] (middle N)	403.7	+0.447	−6.58	(−13.0)
(terminal N)	399.3	−0.723	−18.04	(−16.3)
KCN [d]	399.0	−0.409	−18.00	(−19.3)

a), b), c) They are the same as in Table 3.
d) Calculated as anion.
e) The values in parenthesis are evaluated by non-empirical gross atomic charges in stead of CNDO/2 net charges in Eq. (9). These gross charges have been given in references; R. Bonaccorsi, C. Petorngolo, E. Scrocco, and J. Tomasi, J. Chem. Phys., 48, 1497, 1500 (1968); E. Clementi, ibid., 46, 4731 (1967); W. E. Palke and N. N. Lipscomb, J. Amer. Chem. Soc., 88, 2384 (1966).

bad in certain cases where the corresponding off-diagonal elements of the bond-order matrix are not negligible.

The results calculated by means of Eq. (9) are collected in Tables 3 and 4 for carbon $1s$ and nitrogen $1s$ electrons respectively; they are all shown in Figs. 1 and 2 except for anions. Figures 1 and 2 indicate a rather satisfactory correlation between the observed chemical shifts and the values of $\delta\Delta\varepsilon_s$. The solid lines in Figs. 1 and 2 are inclined about 45°; therefore, it seems that the chemical shifts can be evaluated semi-quantitatively in terms of the $\delta\Delta\varepsilon_s$ in neutral molecules, and that a relation between the molecular-charge distributions and the observed shifts may be in the form of $(Q_A\gamma_{AA}+\sum_{B\neq A}Q_B\gamma_{AB})$. For the anious containing
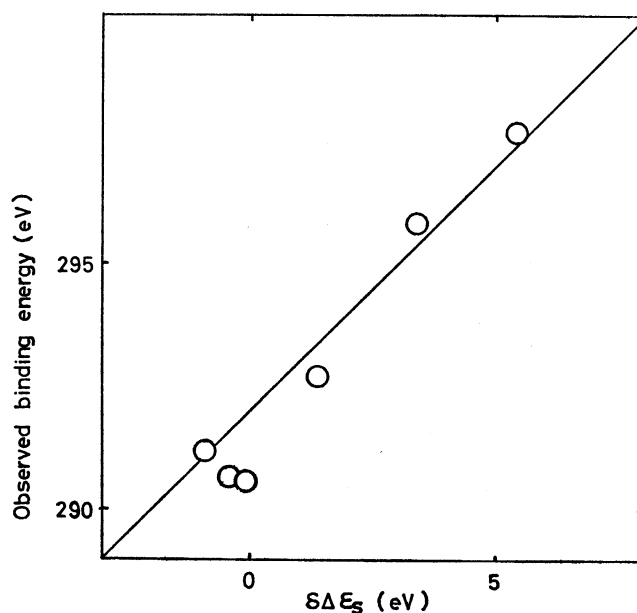

Fig. 1. The observed binding energies of carbon $1s$ electron plotted against the $\delta\Delta\delta_s$'s.
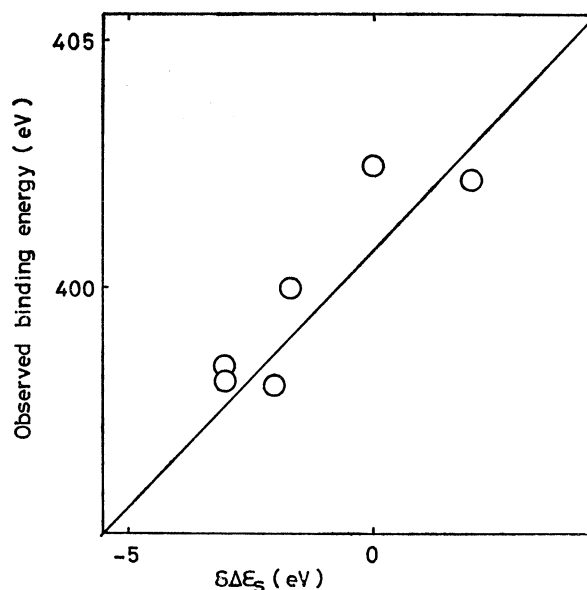

Fig. 2. The observed binding energies of nitrogen $1s$ electrons plotted against the $\delta\Delta\varepsilon_s$'s.

nitrogen atoms, the above rather good correlation is not observed; that is in these charged species, the crystal effects may be considerable.[5]

It is noticed that the values of ε_s obtained by Roothaan's closed-shell treatment are generally larger than those of the binding energy observed at about 10—20%, and open-shell SCF calculations give better results, as has been pointed out by several authors[7-11,13,21,22]. Further it has been suggested that the main effects of these discrepancies depend on the reorganization energy.[19]

Now, let me examine the reorganization energy in the above approximation scheme. Suppose that MO's i and j are given by Roothaan's closed-shell treatment. Using these MO's, an open-shell wave function with an s hole ($S_z = 1/2$), is obtained approximately by a CI scheme;

$$\Phi_s^0 = |s\bar{i}\bar{i}\cdots j\bar{j}| + \sum_{j(\neq s)}^{occ.} \lambda_{is}|s\overline{si}\bar{i}\cdots j| + \sum_k^{vac} \lambda_{sk}|k\bar{i}\bar{i}\cdots j\bar{j}|$$

$$+ \sum_{j(\neq s)}^{occ} \sum_k^{vac} \lambda_{jk}(1)\{|s\bar{i}\bar{i}\cdots j\bar{k}| - |s\bar{i}\bar{i}\cdots \bar{j}k|\}$$

$$+ \sum_{j(\neq s)}^{occ} \sum_k^{vac} \lambda_{jk}(2)\{2|\overline{si}\bar{i}\cdots jk| - |s\bar{i}\bar{i}\cdots j\bar{k}| - |s\bar{i}\bar{i}\cdots \bar{j}k|\}.$$

$$(10)^{23)}$$

That is, Φ_s^0 is an approximate open SCF function[24] and λ_x is the coefficient of a related configuration, x. By perturbation treatment, these are[25];

$$\lambda_{js} = F_{js}/E_{js} = 0, \qquad \lambda_{sk} = \frac{(ks/ss)}{E_{sk}},$$

$$\lambda_{ik}(1) = \frac{\sqrt{2}\{(ik/ss) - (1/2)(is/ks)\}}{E_{ik}(1)},$$

$$\lambda_{ik}(2) = \frac{-\sqrt{3/2}(is/sk)}{E_{ik}(2)}. \qquad (11)$$

Where E_{sk} is the energy difference between the energy of the $s{\to}k$ excited configuration, as shown in Eq. (10), and the ground-state configuration, and so

on.

Then, the energy, E_s^0 becomes;

$$E_s^0 = (E_0 - \varepsilon_s) + \sum_k \frac{(ks/ss)^2}{E_{sk}} + \sum_{k, i\neq s} \frac{2\{(ik/ss) - (1/2)(is/ks)\}^2}{E_{ik}(1)}$$

$$+ \sum_{k, i\neq s} \frac{\{-\sqrt{3/2}(is/ks)\}^2}{E_{ik}(2)} + \cdots \qquad (12)$$

That is, the reorganization energy is $E_s^0 - (E_0 - \varepsilon_s)$, and the dominant contribution comes from the third term, since $E_{sk} \sim \varepsilon_k - \varepsilon_s$(large), $E_{ik}(1) \sim {}^1E_{ik}$ (valence shell $i{\to}k$ singlet excitation energy for a closed-shell system, small), and $(ik/ss) \simeq C_r^i C_r^k (rr/ss)$ is large, and (is/ks) is small as is shown in Table 2.

The magnitude of the third term can be roughly estimated as; E_{sk} (1) ~ 0.5 a.u., $(rr/ss) \sim 1$ a.u., and $\varepsilon_s \sim 10$ a.u.; hence, (the third term)$/\varepsilon_s \sim 10^{-1}$ [26]. This order is reasonable when it is compared with the previous results, $10 \sim 20\%$.[10,13,19,27]

These results indicate that the third part is the most important in reorganization energy. Further, this third term can be approximated:

$$\sum_i \sum_k \frac{2\{\sum_r C_r^i C_r^k (rr/ss)\}^2}{E_{ik}(1)} \sim \sum_B^{all\ on\ B} \sum_r p_{rr}(2 - p_{rr})\frac{(\gamma_{AB})^2}{2E_{av}}$$

Where E_{av} is the average excitation energy.

That is, the reorganization energy is not a linear function for the atomic charges.

As to the other corrections for inner electron binding energies, that is, the correlation correction,[13,28] the relativistic correction[29] and the crystal correction,[3,30] it can be pointed out that these are negligible or are proportional to the charges.

As has been shown in the above discussion, the linear relation between the charges and the inner-shell binding energy is restricted within the imposed approximations; thus, in some cases, this linearities may depend on the cancellations of various effects. We hope this point will be reexamined in the future.

The calculations have been carried out on the FACOM 230—60 Computer of Kyoto University.

21) P. S. Bagus, *Phys. Revs.*, **A619**, 139 (1965).

22) M. E. Schwartz, *Chem. Phys. Lett.*, 5, 50; 6, 631; 7, 78 (1970).

23) The last configuration does not appear in the difference between the zero-th order configuration (the first term) and Roothaan's open SCF configuration. The contribution from this configuration is certainly very small as will be shown later in this report.

24) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

25) For example, R. Zahradnik, and P. Carsky, *J. Phy. Chem.*, **74**, 1235 (1970).

26) The estimated values of the third term in the level of approximations in the present report are, e.g., 22.7 eV for the N_{1s} of pyridine.

27) For valence-electron systems, the same order values are obtained.

28) E. Clementi, *J. Chem. Phys.*, **47**, 4485 (1967).

29) P. Palmiele, and C. Zauli, *Theor. Chim. Acta*, 7, 89 (1967).

30) C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).