The Correspondence between the Molecular Orbital and Differential Ionization Energies Methods[*]

I. The Hydrogen Halides

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The correspondence between Self-Consistent Hückel MO methods and Differential Ionization Energies methods is discussed in terms of the approximations used for the diagonal matrix elements. The two methods are shown to be equivalent if electronic correlation is neglected. Ground-state properties of the hydrogen halides are calculated by these simple methods and shown to be in good overall agreement with experimental data.

Die Übereinstimmung zwischen selbstkonsistenten Hückel MO-Methoden und Methoden der Differentiellen Ionisierungsenergien wird in Termen solcher Näherungen diskutiert, die für die diagonalen Matrixelemente benutzt werden. Es wird gezeigt, daß die beiden Methoden äquivalent sind, wenn die Elektronenkorrelation vernachlässigt wird. Grundzustandseigenschaften der "hydrogen halides" werden mit diesen einfachen Methoden ausgerechnet und zeigen sich in überall guter Übereinstimmung mit experimentellen Daten.

La correspondance entre les méthodes SCF Hückel et d'énergie d'ionisation différentielle est discutée en fonction des approximations utilisées pour les éléments de matrice diagonaux. Les deux méthodes sont équivalentes si la corrélation électronique est négligée. Les propriétés de l'état fondamental des acides halogénés sont calculées par ces méthodes simples et l'on constate un accord raisonnable avec les données expérimentales.

The purpose of this paper is to analyze the correspondence between Self-Consistent Hückel (SCHMO) methods [1–3] and the Differential Ionization Energies (DIE) calculations [4–7]. This problem has been dealt with by Jørgensen, Horner, Hatfield, and Tyree [4], and by Klopman [8], but it is presented here in a more general way, together with calculations for the ground-state properties of the hydrogen halides. These can be compared with SCF-LCAO-MO calculations of σ-bonded systems [9–11].

1. Self-Consistent Hückel Methods

Let φ_i and φ_j be the valence orbitals of atoms A and B, respectively. We describe a doubly occupied MO as:

$$\Psi_m = c_i \varphi_i + c_j \varphi_j. \tag{1}$$

The operator of $H_{ii} = \langle \varphi_i \mathscr{H} \varphi_i \rangle$ includes the interaction of one electron centered in φ_i with all other nuclei and electrons, including the other electron in the molecular orbital Ψ_m. The diagonal elements may be partitioned by Mulliken's approximation [12]:

$$H_{ii} = \varepsilon_i + V_{ij} + c_i^2 J_{ii} + c_j^2 J_{ij} \tag{2}$$

where $\varepsilon_i = \left\langle \varphi_i^*(1) \left| -\frac{1}{2} V_1^2 - \frac{1}{r_{1i}} \right| \varphi_i(1) \right\rangle$ is the atomic one-electron eigenvalue. ε_i is equal to $-I_i$, that is, to the VOIP (or VSIP) corresponding to the atomic orbital φ_i. V_{ij} lumps together the core integrals $\langle \bar{u}_j \varphi_i^* \varphi_i \rangle$ and J_{ii} and J_{ij} are the two-electron Coulomb integrals. We further assume [13, 14] that $J_{ii} = I_i - A_i$, where A_i is the valence-state electron affinity (VSEA). Eq. (2) can be written:

$$H_{ii} = -I_i + c_i^2(I_i - A_i) + V_{ij} + c_j^2 J_{ij}. \tag{3}$$

The first two terms in the right-hand side of (3) are the *atomic terms*, the others the *molecular terms* of H_{ii}. The latter corresponds to an interatomic Coulomb correction, and has been called the Madelung-Jørgensen potential [15]. The charge dependence of the parameters H_{ii} and H_{ij} must be included in the differentiations leading to the minimum-energy condition. This important point has been recently stressed by Harris [16].

The form of the atomic terms in (3) is identical to Moffitt's approximation [13], and it is also consistent with the SCF matrix element formulation [1]. The atomic orbital energy function derived from the atomic terms of Eq. (3) is:

$$\varepsilon_i(n_i) = -I_i n_i + 1/4 \, n_i^2 (I_i - A_i) \tag{4}$$

where $n_i = 2c_i^2$ is the occupation number of orbital φ_i. The quantum mechanical expression for the energy of an isolated atomic orbital is, on the other hand:

$$\varepsilon_i(n_i) = -I_i n_i + 1/2 \, n_i(n_i - 1)(I_i - A_i). \tag{5}$$

The difference (4)–(5) corresponds to the right-left correlation energy [17], which is entirely neglected in simple MO theory. It will be shown in Sect. 3 that Eq. (4) is the only atomic energy function that leads to a complete equivalence between the SCHMO and the DIE methods.

We assume that the point charge description [18] holds and if $c_i^2 = 1 - c_j^2$, Eq. (3) transforms to:

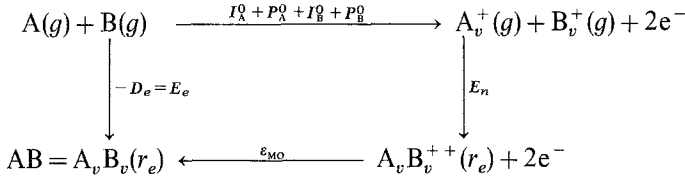$$H_{ii} = -I_i + c_i^2(I_i - A_i) - c_i^2 \frac{e^2}{r_{ij}}. \tag{6}$$

The off-diagonal matrix elements are calculated by an equation of the type:

$$H_{ij} = K S_{ij}(H_{ii} + H_{jj})/2. \tag{7}$$

The procedure, however, is not strictly a Wolfsberg-Helmholz calculation because overlap integrals are neglected in the secular equations. As a result, the value of

K in Eq. (7) can be freely varied without the associated dangers of inversion of the energy levels [19–23].

Eq. (6) is the correct diagonal matrix element for the calculation of one-electron properties of AB systems, such as ionization potentials. Bond energies, force constants, dipole moments, etc., are, however, electron-pair properties and expression (6) must be modified. From the cycle:

$$A(g) + B(g) \xrightarrow{\;I_A^0 + P_A^0 + I_B^0 + P_B^0\;} A_v^+(g) + B_v^+(g) + 2e^-$$

$$\left\downarrow{\scriptstyle -D_e = E_e}\right. \qquad\qquad\qquad \left\downarrow{\scriptstyle E_n}\right.$$

$$AB = A_v B_v(r_e) \xleftarrow{\quad \varepsilon_{MO} \quad} A_v B_v^{++}(r_e) + 2e^-$$

we have:

$$E_e = -D_e = \varepsilon_{MO} + E_n + I_A^0 + P_A^0 + I_B^0 + P_B^0. \tag{8}$$

With the usual conventions, $D_e > 0$; E_e is simply $-D_e$, and binding occurs only if $\varepsilon_{MO} < 0$ and $|\varepsilon_{MO}| > (E_n + I_A^0 + P_A^0 + I_B^0 + P_A^0)$. E_n is the core-core repulsion energy; in our calculations $E_n = \dfrac{Z_A Z_B}{r_{AB}}$, where Z_A and Z_B are the effective charges seen by a unit charge at the distance r_{AB} from A and B, respectively. We may write

$$E_n = \frac{Z_A Z_B}{r_{AB}} = \frac{e^2}{r_{AB}} + \frac{(Z_A Z_B - e^2)}{r_{AB}} \tag{9}$$

where the first term in the right-hand side is the Coulomb repulsion between A_v^+ and B_v^+, and $\dfrac{(Z_A Z_B - e^2)}{r_{AB}}$ is a penetration term. A_v and B_v refer to the valence states, and P_A^0 and P_B^0 are the promotion energies. Since the H_{ii} and H_{ij} integrals are one-electron integrals, the Hamiltonian for the process $AB \rightarrow AB^+ + e^-$ is different from the Hamiltonian for the process $AB^+ \rightarrow AB^{++} + e^-$. In the latter, there is no screening potential from the second electron [12]. We have:

$$H_{ii}(1) = -I_i + c_i^2(I_i - A_i) - c_i^2 \frac{e^2}{r_{ij}}, \tag{6a}$$

$$H_{ii}(2) = -I_i - \frac{e^2}{r_{ij}}. \tag{6b}$$

The diagonal matrix elements to be used for the calculation of two-electron properties is the average value:

$$H_{ii} = -I_i + \frac{c_i^2}{2}(I_i - A_i) - \frac{(1 + c_i^2)}{2} \frac{e^2}{r_{ij}}. \tag{10}$$

Eq. (10) and (7) give the correct one-electron integrals, and for the doubly occupied MO:

$$\varepsilon_{MO} = 2[c_i^2 H_{ii} + c_j^2 H_{jj} + 2c_i c_j H_{ij}]. \tag{11}$$

For the usual equilibrium internuclear distance, the terms $(I_i - A_i)$ and $\dfrac{e^2}{r_{ij}}$ are of comparable magnitude and this [8] explains the success of SCCC-LCAO-MO methods in which one assumes [4] that $H_{ii} = -(\text{VSIP})_i$. Also, because Eq. (10) shows a small dependence of H_{ii} on c_i^2, we can explain the use of the hydride or neutral atom ionization energies for the diagonal elements of ligand *ions* in complexes [24].

2. The Differential Ionization Energies Method

In this method [4-7], the bond energy is given by a sum of atomic and interatomic terms expressed as functions of the *atomic charges* and, for the latter terms, of the *bond distances*. The relation between the occupation numbers of the orbitals φ_i and φ_j and the bond *ionicity* χ depends on the way the orbital populations are defined. In our case, $S_{ij} = 0$, and since $n_i + n_j = 2$, we have $\chi = n_i - 1 = c_i^2 - c_j^2 = 2c_i^2 - 1$. For the atomic energy terms, it is customary [4, 5, 7, 8, 25, 26] to use Eq. (5). We will show in the next section that the DIE method is equivalent to the SCH-MO method only if we use Eq. (4) for the atomic orbital energy terms. This means that for the separated atoms, or for a purely covalent bond $(x = 0)$, we are including too much electron repulsion. We also must change coordinates since now $\varepsilon_i(0) = +I_i$, $\varepsilon_i(1) = 1/4(I_i - A_i)$, and $\varepsilon_i(2) = -A_i$, corresponding to $\chi = -1, 0,$ and $+1$. Since $n_i = 2c_i^2 = x + 1$ and $n_j = 2c_j^2 = 1 - x$, Eq. (4) can now be written:

$$\varepsilon_i(x) = 1/4(I_i - A_i) - 1/2(I_i + A_i)\,x + 1/4(I_i - A_i)\,x^2 = \varepsilon_i(n_i) + I_i, \qquad (12a)$$

$$\varepsilon_j(x) = 1/4(I_i - A_i) + 1/2(I_j + A_j)\,x + 1/4(I_j - A_j)\,x^2 = \varepsilon_j(n_j) + I_j. \qquad (12b)$$

In this paper, we will suppose that $|F_{ii}| > |F_{jj}|$ (F_{ii} represents the Hartree-Fock matrix elements; see Sect. 3), and hence x is always positive. The interatomic term is described by the sum of a covalent and an ionic bond energy, each one multiplied by the corresponding bond-order [7, 27]. The covalent bond order is $2c_ic_j = (1 - x^2)^{1/2}$, the ionic bond order is x^2. The ionic bond energy is $-\dfrac{e^2}{r_{ij}}$. Several approximations can be used for the covalent bond energy E_c, and our particular choice will be discussed in Sect. III. Thus, the bond energy function is:

$$E_e(x) = (1 - x^2)^{1/2} E_c - x^2 \frac{e^2}{r_{ij}} + \varepsilon_i(x) + \varepsilon_j(x) + \mathscr{R}. \qquad (13)$$

$\varepsilon_i(x)$ and $\varepsilon_j(x)$ are given by Eq. (12a) and (12b), and $\mathscr{R}$ is the repulsive penetration term for the approaching atoms and given by $\mathscr{R} = \dfrac{Z_a Z_b - e^2}{r_{ij}}$.

For any reasonable value of r_{ij}, $E_e(x)$ is negative and, in fact, the bond energy is $D_e = -E_e(x_e)$.

Bond energies are calculated by minimizing $E(x)$ with respect to x. One must decide what approximation to use for E_c, the covalent bond energy. The arith-

metic and geometrical mean rules cannot be used, because they include the penetration term, whereas in Eq. (13), this term is shown explicitly. We will show in the next section that the point charge approximation leads to $E_c = \left(2H_{ij} - \dfrac{e^2}{r_{ij}} c_i c_j\right)$, where H_{ij} is the off-diagonal matrix element. With this approximation, $E(x)$ may be written as:

$$E(x) = \left[2H_{ij} - \frac{e^2}{2r_{ij}}(1-x^2)^{1/2}\right](1-x^2)^{1/2} - x^2 \frac{e^2}{r_{ij}} + \varepsilon_i(x) + \varepsilon_j(x) + \mathscr{R}. \tag{13a}$$

Accordingly:

$$\frac{dE(x)}{dx} = -\frac{x}{(1-x^2)^{1/2}}\left(2H_{ij} - x\frac{e^2}{r_{ij}}\right) - 1/2(I_i + A_i) + 1/2(I_i - A_i)x$$

$$+ 1/2(I_j + A_j) + 1/2(I_j - A_j)x = 0 \tag{14}$$

and hence'

$$x_e = \frac{X_i - X_j}{-2H_{ij}(1-x^2)^{-1/2} - \dfrac{e^2}{r_{ij}} + 1/2(I_i - A_i) + 1/2(I_j - A_j)} \tag{15}$$

where $X_i = 1/2(I_i + A_i)$ and $X_j = 1/2\,(I_j + A_j)$. x_e is, of course, a function of r_{ij}. Eq. (15) is identical to Eq. (32) of Jenkins and Pedley [11], which shows the correspondence between the two methods. It should be pointed out that Eq. (15) was derived from Eq. (4) and corresponds to complete neglect of correlation. As a result, Eq. (15) gives too high values for x_e. Eq. (5) on the other hand overestimates correlation and leads to an equation identical to (15) except that the terms $(I - A)$ in the denominator appear with coefficients of one, instead of 1/2.

The relative merits of the two approaches have been discussed by Baird, Sichel, and Whitehead [28].

3. The Equivalence between the SCHMO and DIE Methods

The equivalence between the self-consistent method in Hückel theory and the DIE method can be established from the fact that the following identity holds:

$$\begin{aligned}
-D_e = E(x) = &\left(2H_{ij} - 1/2(1-x^2)^{1/2}\frac{e^2}{r_{ij}}\right)(1-x^2)^{1/2} - x^2 \frac{e^2}{r_{ij}} \\
&+ 1/4(I-A)_i - 1/2(I+A)_i x + 1/4(I-A)_i x^2 + 1/4(I-A)_j \\
&+ 1/2(I+A)_j x + 1/4(I_j - A_j)x^2 + \frac{Z_a Z_b - e^2}{r_{ij}} \\
\equiv\ & 2c_i^2\left[-I_i + c_i^2/2(I-A)_i - (1+c_1^2)/2e^2/r_{ij}\right] \\
&+ 2c_j^2\left[-I_j + c_j^2/2(I-A)_j - (1+c_j^2)/2e/r_{ij}\right] \\
&+ 2(2c_i c_j)H_{ij} + \frac{Z_a Z_b}{r_{ij}} + I_A^0 + P_A^0 + I_B^0 + P_A^0.
\end{aligned} \tag{16}$$

The identity (16) holds provided $x = c_i^2 - c_j^2 (S_{ij} = 0)$. It also depends on the identification of E_c with $\left[2H_{ij} - c_1 c_2 \dfrac{e^2}{r_{ij}} \right]$. It is sometimes assumed that $E_c = 2H_{ij}$; but this is only true if we drop the Coulomb interatomic terms in the diagonal elements.

Harris [16] has recently drawn the attention to an important point: in minimizing ε_{MO} with respect to the variational coefficients the charge dependence of H_{ii} and H_{ij} must be included. That is, the correct eigenvalue equations are:

$$c_1(F_{11} - \varepsilon) + c_2(F_{12}) = 0, \qquad c_1(F_{12}) + c_2(F_{22} - \varepsilon) = 0 \tag{17}$$

where

$$F_{11} = H_{11} + \frac{c_1^2}{2} \left[(1 - A)_1 - \frac{e^2}{r_{ij}} \right] = -I_1 + c_1^2(I - A) - \frac{e^2}{r_{ij}} \frac{(1 + 2c_1^2)}{2} \tag{17a}$$

and

$$F_{12} = H_{12} + c_1^2 \frac{K S_{12}}{4} \left[(I - A)_1 - \frac{e^2}{r_{ij}} \right] + \frac{c_2^2}{4} K S_{12} \left[(I - A) - \frac{e^2}{r_{ij}} \right] \tag{17b}$$

which, on the one hand, corresponds exactly to the system of Eq. (9) of Harris [16] and, on the other hand, to the minimization procedures of the DIE method leading to Eq. (15) and hence to the energy function (13) above.

4. The Hydrogen Halides: Results and Discussion

The main points in the calculation of ground state properties of the hydrogen halides are as follows: F_{11}, F_{22} and F_{12} were given by (17a) and (17b); H_{12} is given by (7); the best value of K in Eq. (7) was found by trial to be 0.4. Since the calculation is not a Wolfsberg-Helmholz treatment, no special significance should be assigned to the chosen value of K. Overlap integrals in Eq. (7) are from Mulliken, Rieke, Orloff, and Orloff [29], and $S(4p, 1s)$ values are interpolated from $S(3p, 1s)$ and $S(5p, 1s)$. Self-consistent solutions of Roothaan Eq. (17) were attained by the usual procedures [9, 30]. Core-core repulsions, E_n, are calculated by the method suggested by Pohl and Raff [10], $E_n = \dfrac{Z_A Z_B}{r_{ij}}$, where Z_A and Z_B are estimated from the Herman-Skillman atomic structure tables [31]. Valence state ionization energies and electron-affinities are from Hinze and Jaffe [32]. Calculations were made with an IBM 1130 computer.

Calculated and experimental [33–36] ground-state properties of the hydrogen halides are given in the table and the calculated potential curves for these four molecules are shown in Fig. 1. In general, the calculated values are in reasonable agreement with the experimental ones. The trend in dissociation energies, equilibrium internuclear distances, bond dipole moments, dipole moment functions and force constants is the correct one throughout the series HX. As predicted,

Table

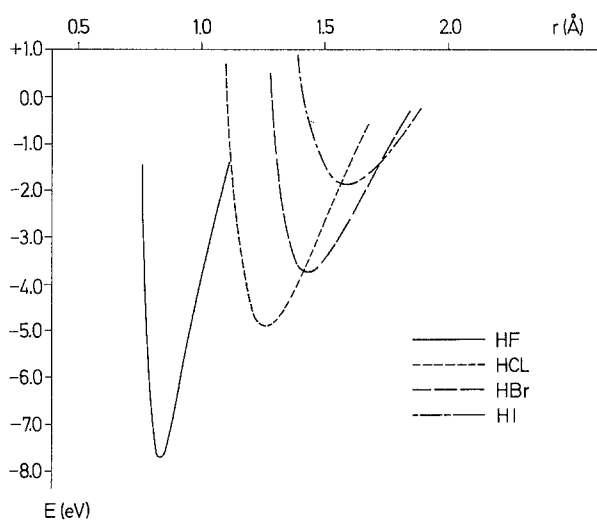|	HF	HCl	HBr	HI	Ref.
D_e(calc) (eV)	7.59	4.84	3.73	1.85	
D_e(exp) (eV)	6.08	4.47	3.80	3.10	[33]
R_e(calc) (Å)	0.87	1.30	1.48	1.64	
R_e(exp)(Å)	0.917	1.275	1.414	1.604	[33]
χ_e(calc)	0.68	0.26	0.16	0.075	
μ_{prim}(calc) (D)	3.26	1.24	0.77	0.36	
μ(exp) (D)	1.82	1.08	0.82	0.44	[34]
$\left(\dfrac{\partial \mu}{\partial r}\right)_{re}$ (calc) (D/Å)	+2.12	+1.08	+0.71	+0.36	
$\left(\dfrac{\partial \mu}{\partial r}\right)_{re}$ (exp) (D/Å)	+1.8	±1.0	±0.9	±0.2	[35, 36]
k(calc) (dynes/cm)	20.2×10^5	4.6×10^5	2.5×10^5	1.1×10^5	
k(exp) (dynes/cm)	9.6×10^5	5.1×10^5	4.1×10^5	3.1×10^5	[33]

Fig. 1. Potential curves of the hydrogen halides

function (4) tends to introduce a high ionicity, and this is reflected in the high values of the calculated dipole moments of HF and HCl. Actually, these values represent the primary moments only, the total dipole being the sum of the primary and the homopolar moments. The calculated values of $\left(\dfrac{\partial \mu}{\partial r}\right)_{re}$ are in good agreement with the experimental ones. They are also in general accord with

dipole moment functions calculated (for HF and HCl) using advanced SCF techniques [37]. There is little doubt that the sign of $\left(\dfrac{\partial \mu}{\partial r}\right)$ at the equilibrium distance is positive and that for ordinary chemical bonds the stationary value of the bond moment occurs at distances larger than the equilibrium internuclear distances. This is true in our calculation although $\left(\dfrac{dx}{dr}\right)$ is always negative.

The calculated bond energies and force constants are too large for HF, and too small for HI. There is little doubt that the point charge approximation as used here over-emphasizes the Madelung-Jørgensen energy terms in F_{11} [8]. Because of polarization effects, the charges should not be located at the nuclear centers. Corrections along these lines would undoubtedly produce better results, notably for hydrogen fluoride, but at the expense of one more arbitrary parameter.

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