ab initio Evaluation of the α, β, K, ω Parameters of the Semiempirical Theories I: Spin Restricted Version

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ABSTRACT

The ab initio calculations of the α, β, K, ω Parameters of the Wolfberg - Helmholz's and Wheland & Mann's semiempirical theories are presented for a generalized closed shell system at a zeroth order level. The K and ω quantities now have firm literal basis and clearly defined physical meaning, contrary to the conclusion of the ab initio theorist that they are ill-founded parameters.

INTRODUCTION

The emergence of *superspeed* computers and the availability of programs have made it possible to perform *ab initio* calculations beyond the Hartree-Fock level[1]. However, it has been generally recognized that the *ab initio* wavefunctions generated from such calculations are often difficult to interprete in chemical terms. Also, the question of *accuracy* for certain properties of large molecules still persists even with the largest basis set possible beyond the valence shell.

Notwithstanding this considerable progress in the direction of *ab initio* methods, semiempirical calculations could be performed with relative ease and the results stay closer to experimental chemistry in dealing with the properties of classes of molecules rather than individual molecules. In addition, they relate integrals that occur in quantum chemistry directly to the properties of atoms and molecules. Despite the much celebrated successes of the semiempirical theories, some *ab initio* theorists hold the view that they are rather ill-founded and parameter fitting techniques. But the question is why does the semiempirical theory often work better than the former even though its wavefunction has no apparent literal counterpart in the solutions of the full Schrödinger equation? These, in our opinion, are sufficient justification for the continued interest in semiempirical methods[2-8].

The adjustable parameters of the semiempirical theories are basically the integrals not canceled by the theories' levels of approximations. While two- and multi-electron integrals are calculated in most cases, the one-electron integrals are optimized from experimental data through empirical expressions. Of the one-electron integrals, the bond integral H_{kl} is the most crucial. It has always been treated as an adjustable parameter set proportional to the overlap through Mulliken's magic formula[9]

$$H_{KL} \cong S_{kl}\beta_{kl} \quad \text{..................................(1)}$$

where the proportionality constant β_{kl} is assumed to be a function only of the nature of the bonded atoms, fragments, molecules, etc. to which orbitals k and l are located.

In the extended Hückel theory (EHT) formalism, for example, the Wolfberg - Helmholz[10] relation

$$\beta_{kl} = K\frac{(\alpha_k + \alpha_l)}{2} \quad \text{..........................(2)}$$

is used to express this constant, α_k and α_l being parameters characteristic of the bonded atoms, fragments, molecules, etc. only that are determined empirically. The coefficient K is an adjustable parameter that has no theoretical basis and, in general, agreement with experiment depends upon the best choice for its value. In almost all reported cases K lies in the range

$$0 < K < 2 \quad \text{..................................(3)}$$

Whilst the bond integral H_{kl} is conveniently optimized and related to the intermolecular distance by the Mulliken's magic formula in most semiempirical theories, there have been so many variant formulas for the determination of the diagonal matrix element H_{kk}. Of the various forms, the Wheland & Mann's expression[11],

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$$H_{kk} = (1+\omega)\alpha_k , \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

is the most reliable. The parameter ω is intended to take care of charge deflation on moieties. Thus, both K and ω have no literal meaning; they are the empirical parameters which make the semiempirical theories that use the parametric expressions (2) and (4) work.

But assigning experimental values to quantum mechanical integrals, such as H_{kk} and H_{kl} in equations (1), (2) and (4) etc., ought to force us to examine the theoretical basis of the parametric expressions of the semiempirical theories. On this issue, only feeble attempts were made in the literature to interprete the parameters α, β, K, ... in terms of *ab initio* theory. For instance, by choosing a model Hamiltonian to correspond with the true effective valence shell Hamiltonian, Iwata and Freed[12] evaluated the parameters α, β, γ of the PPP semiempirical π-electron theory for ethylene from first principles. Also, Carbo and Arnau[13] proved the mathematical basis of equation (2) above for the special case of $K = 1$. Taking it all in all, these works are scarce because it is a daunting task in many cases. Even for the cases reported, the theoretical bases proved were not generalized. In fact, most systems have $K \neq 1$. Furthermore, the work of Carbo and Arnau could not attach any physical meaning to the K parameter. But of course even this kind of attempt to provide some literal basis is difficult to cite for ω.

In this study, the *ab initio* calculations (i.e. literal interpretation) of the α, β, K, ω parameters of the H_{kk} and H_{kl} integrals of the extended Hückel semiempirical theory and Wheland & Mann's formula (4) are presented for a generalized cases of atoms, fragments, molecules, etc. at the zeroth order approximation for any electron system. In particular, the mathematical expressions derived for K and ω reveal defined physical meanings. The work is, however, divided into two parts: in the present paper, the derivations reported are for spin - restricted systems whilst in the next one (same issue of this journal) the case of spin-polarized systems is examined. Ruedenberg's approximations[14] is employed in the calculations.

ab initio DERIVATION OF THE α, β, K, ω SEMIEMPIRICAL PARAMETERS: SPIN RESTRICTED VERSION

For the sake of flow and completeness, we shall review some essential standards. That is, using the true Hamiltonian with one- and two-electron operators and a zeroth order closed shell wave function $\Psi(1, 2, \ldots, N)$ it can be shown that the one-electron molecular orbitals $\{\psi_p ; p = 1, 2, \ldots\}$ of the $\Psi(1, 2, \ldots, N)$ satisfy

$$H_i\psi_p(i) = \varepsilon_p\psi_p(i) \qquad p = 1,2,\ldots\ldots \quad \ldots.(5)$$

Hartree - Fock - Roothan equations, H_i being one-electron operators. The molecular orbitals $\{\psi_p ; p = 1, 2, \ldots\}$ may be expanded as linear combination of independent funtions $\{\phi_{au}, \phi_{bn}, \phi_{cm}, \phi_{dw}, \ldots; a, b, c, d, \ldots; u, n, m, w, \ldots\}$

$$\psi_p = \sum_a \sum_k C_{pak}\phi_{ak} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where the indices a, b, c, d, ...denote atoms, fragments, molecules, etc. whereas u, n, m, w, ... denote basis set orbitals on the a, b, c, d, ... moieties. Putting (6) in (5), the trial one-electron energies become

$$\varepsilon_p = \sum_a \sum_k \sum_b \sum_l C^*_{pak} C_{pbl} H_{ak,bl} \Big/ \sum_a \sum_k \sum_b \sum_l \times C^*_{pak} C_{pbl} S_{ak,bl} \qquad \ldots\ldots\ldots\ldots\ldots(7)$$

From (7), it is easy to show that the values of C^*_{pak} which give the lowest value for the ε_p and therefore the best approximation to the total energy, $E = 2\Sigma_p\varepsilon_p$, $p = 1, 2, \ldots$ (occupied MOs), satisfy

$$\sum_b \sum_l C_{pbl}(H_{ak,bl} - \varepsilon_p S_{ak,bl}) = 0 \quad , \quad \ldots\ldots(8)$$

for each a and k as condition for minimum. The $S_{ak,bl}$ and $H_{ak,bl}$ are defined as

$$S_{ak,bl} = \int \phi^*_{ak}\phi_{bl}d\tau \text{ , and} \qquad \ldots\ldots\ldots\ldots\ldots(9)$$

$$H_{ak,bl} = \left\langle \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}} \right| \phi_{bl} \right\rangle + \sum_c \sum_m \sum_d \sum_w \times \frac{P_{cm,dw}}{2}\left(\langle \phi_{ak}\phi_{bl} | \phi_{cm}\phi_{dw} \rangle - \frac{1}{2} \langle \phi_{ak}\phi_{dw} | \phi_{bl}\phi_{cm} \rangle \right)$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

where

$$P_{cm,dw} = 2\sum_{q} C^{*}_{qcm} C_{qdw} \quad \text{..............}(11)$$

It should be noted that in equation (10) we could have $H_{ak,ak}$ (or simply H_{kk}) when $k = l$ and $a = b$. Also, this equation has been the starting point of all the rigorous semiempirical spin-restricted theories. We too shall begin from it.

Evaluation of Wheland & Mann's parameters α and ω

From (10) the diagonal matrix elements, i.e. the case $a = b$ and $k = l$, are

$$H'_{ak,ak} = <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}}\right|\phi_{ak}> + \sum_c \sum_m \sum_d \sum_w$$

$$\times \frac{P_{cm,dw}}{2}\left(<\phi_{ak}\phi_{ak}\middle|\phi_{cm}\phi_{dw}> - \frac{1}{2}<\phi_{ak}\phi_{dw}\middle|\phi_{ak}\phi_{cm}>\right)$$

$$= <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}}\right|\phi_{ak}> + \sum_u \frac{P_{au,au}}{2}(<\phi_{ak}\phi_{ak}$$

$$\times \left|\phi_{au}\phi_{au}> - \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right) + \sum_u \sum_{c\neq a} \sum_m \frac{P_{cm,au}}{2}$$

$$\times \left(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{cm}> - \frac{1}{2}<\phi_{ak}\phi_{cm}\middle|\phi_{ak}\phi_{au}>\right)$$

$$+ \sum_{c\neq a} \sum_m \sum_{d\neq a} \sum_w \frac{P_{cm,dw}}{2}(<\phi_{ak}\phi_{ak}\middle|\phi_{cm}\phi_{dw}>$$

$$- \frac{1}{2}<\phi_{ak}\phi_{dw}\middle|\phi_{ak}\phi_{cm}>) \quad \text{........................}(12)$$

Equation (12) contains two- and multicentre-electron integrals which are very difficult to handle computationally. For that reason, we employ the Ruedenberg's approximation[14], which was mathematically justified[13], to transform all two- and multicentre-electron integrals into one-centre integrals that can be managed without loss of accuracy. Making use of the approximation, namely expanding

$$\phi_{oj} = \sum_{r=1}^{\infty} S_{oj,ar}\phi_{ar}, \quad o = c,d,\ldots;\ j = m,w,\ldots \quad (13)$$

and setting the overlap charge density $\phi'_{at}(i)\phi_{ar}(i) = \delta_{tr}$, equation (12) becomes

$$H_{ak,ak} = <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}}\right|\phi_{ak}> + \sum_u \frac{P_{au,au}}{2}(<\phi_{ak}\phi_{ak}$$

$$\times \left|\phi_{au}\phi_{au}> - \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right)$$

$$+ \sum_u \sum_{c\neq a} \sum_m \frac{P_{cm,au}}{2} S_{cm,au}(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}>$$

$$- \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>) + \sum_u \sum_{c\neq a} \sum_m \sum_{d\neq a} \sum_w \frac{P_{cm,dw}}{2}$$

$$\times S_{cm,au}S_{dw,au}(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}> - \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>) \quad (14)$$

Further, we manipulate (14) by adding

$$\sum_u \left(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}> - \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right) \quad (15)$$

to it and subtracting same from it (operation nothing). We got

$$H_{ak,ak} = <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}}\right|\phi_{ak}> + \sum_u (<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}>$$

$$- \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>) + \sum_u \left(\frac{P_{au,au}}{2} + \sum_{c\neq a} \sum_m \frac{P_{cm,au}}{2} S_{cm,au}\right.$$

$$\left. + \sum_{c\neq a} \sum_m \sum_{d\neq a} \sum_w \frac{P_{cm,dw}}{2} S_{cm,au}S_{dw,au} - 1\right)$$

$$\left(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}> - \frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right) \quad (16)$$

Again, the second term of (16) can be difficult to control. So, we made the following additional approximation

$$\frac{P_{au,au}}{2} + \sum_{c\neq a} \sum_m \frac{P_{cm,au}}{2} S_{cm,au} + \sum_{c\neq a} \sum_m \sum_{d\neq a} \sum_w \frac{P_{cm,dw}}{2}$$

$$\times S_{cm,au}S_{dw,au} - 1$$

$$\cong \frac{P_{ak,ak}}{2} + \sum_{c \neq a} \sum_{m} \frac{P_{cm,ak}}{2} S_{cm,ak} + \sum_{c \neq a} \sum_{m} \sum_{d \neq a} \sum_{w}$$

$$\times \frac{P_{cm,dw}}{2} S_{cm,ak} S_{dw,ak} - 1 \quad \ldots\ldots\ldots\ldots(17)$$

all u index. Inserting (17) in (16) we have

$$H_{ak,ak} = < \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}} \right| \phi_{ak} > + \sum_u (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} >$$

$$-\frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >) + \left(\frac{P_{ak,ak}}{2} + \sum_{c \neq a} \sum_{m} \frac{P_{cm,ak}}{2} S_{cm,ak} \right.$$

$$\left. + \sum_{c \neq a} \sum_{m} \sum_{d \neq a} \sum_{w} \frac{P_{cm,dw}}{2} S_{cm,ak} S_{dw,ak} - 1 \right)$$

$$\times \sum_u (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >)$$

$$= (1 + \omega_{ak})\alpha_{ak} \quad \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

where the α_{ak}'s are basis orbital energies which depend only on the nature of the *a*th moiety. They are defined by

$$\alpha_{ak} = < \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}} \right| \phi_{ak} > + \sum_u (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} >$$

$$-\frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >)$$

$$= I_{ak,ak} + \sum_u (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \frac{1}{2} < \phi_{ak}\phi_{ak}$$

$$\times | \phi_{ak}\phi_{au} >) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

and

$$\omega_{ak} = \left(\frac{P_{ak,ak}}{2} + \sum_{c \neq a} \sum_{m} \frac{P_{cm,ak}}{2} S_{cm,ak} + \sum_{c \neq a} \sum_{m} \sum_{d \neq a} \sum_{w} \right.$$

$$\left. \times \frac{P_{cm,dw}}{2} S_{cm,ak} S_{dw,ak} - 1 \right) \frac{\alpha_{ak} - I_{ak,ak}}{\alpha_{ak}} \quad \ldots(20)$$

The parameter ω_{ak} is a function of charge $P_{ak,ak}$ as well as bond orders $\{P_{cm,ak}$ and $P_{dw,ak}$; c and d $\neq a\}$. It should be noted, however, that ω_{ak} in (20) is mainly due to the charge $P_{ak,ak}$ so that ($P_{ak,ak}/2 - 1$) accounts for charge deflation on the *a*th moiety due to an electron in orbital ϕ_{ak} exactly as in the Wheland & Mann's semiempirical theory.

Evaluation of the Wolfberg - helmholz's parameters K and β

The off-diagonal matrix elements $H_{ak,bl}$ are given by (10). Again, making use of the Ruedenberg's approximation, i.e.

$$\phi_{oj} = \sum_{r=1}^{\infty} S_{oj,ar}\phi_{ar}, \quad o = a,b,c,d,; \; j = k,l,m,w, \quad (21)$$

and setting the overlap charge density $\phi_{at}(i)\phi_{ar}(i) = \delta_{tr}$, we obtain

$$H_{ak,bl} = S_{bl,ak}\{< \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_a \frac{Z_a}{r_{ai}} \right| \phi_{ak} > + \sum_u \sum_n \frac{P_{au,bn}}{2}$$

$$\times (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >)$$

$$+ \sum_{c \neq a,b} \sum_{m} \sum_{u} \left(\frac{P_{cm,au}}{2} S_{cm,au} + \sum_n \frac{P_{cm,bn}}{2} S_{cm,au} S_{bn,au} \right)$$

$$\times (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >)$$

$$+ \sum_{c \neq a,b} \sum_{m} \sum_{d \neq a,b} \sum_{w} \sum_{u} \frac{P_{cm,dw}}{2} S_{cm,au} S_{dw,au}$$

$$\times (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \frac{1}{2} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >)\} \quad \ldots(22)$$

The second and third terms in (22) are easily handled if, as in the case of $H_{ak,ak}$, we use the approximation of (17) to estimate them. That is

$$\text{(i)} \quad \sum_n \frac{P_{au,bn}}{2} S_{bn,au} \cong \sum_n \frac{P_{ak,bn}}{2} S_{bn,ak}, \quad \ldots\ldots(23)$$

$$\text{(ii)} \sum_{c \neq a,b} \sum_{m} \left(\frac{P_{cm,au}}{2} S_{cm,au} + \sum_n \frac{P_{cm,bn}}{2} S_{cm,au} S_{bn,au} \right)$$

$$\cong \sum_{c\neq a,b}\sum_{m}\left(\frac{P_{cm,ak}}{2}S_{cm,ak}+\sum_{n}\frac{P_{cm,bn}}{2}S_{cm,ak}S_{bn,ak}\right) \quad (24)$$

and

$$\text{(iii)}\quad \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,au}S_{dw,au}$$

$$\cong \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,ak}S_{dw,ak} \quad .....(25)$$

all u index. Putting (23) to (25) in (22) the bond integral simplifies to

$$H_{ak,bl} = S_{bl,ak} < \phi_{ak}\left|-\frac{\nabla_i^2}{2}-\sum_{a}\frac{Z_a}{r_{ai}}\right|\phi_{ak} > +S_{bl,ak}\left\{\sum_{n}\frac{P_{ak,bn}}{2}\right.$$

$$\times S_{bn,ak}+\sum_{c\neq a,b}\sum_{m}\left(\frac{P_{cm,ak}}{2}S_{cm,ak}+\sum_{n}\frac{P_{cm,bn}}{2}S_{cm,ak}S_{bn,ak}\right)$$

$$\left.+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,ak}S_{dw,ak}\right\}$$

$$\times\sum_{u}\left(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}>-\frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right) \quad ..(26)$$

Also, if we add

$$S_{bl,ak}\sum_{u}\left(<\phi_{ak}\phi_{ak}\middle|\phi_{au}\phi_{au}>-\frac{1}{2}<\phi_{ak}\phi_{au}\middle|\phi_{ak}\phi_{au}>\right) \quad ....(27)$$

to (26) and subtract same from it (operation nothing) the result will be

$$H_{ak,bl} = S_{bl,ak}\left[\alpha_{ak}+\left\{\sum_{n}\frac{P_{ak,bn}}{2}S_{bn,ak}+\sum_{c\neq a,b}\sum_{m}\right.\right.$$

$$\times\left(\frac{P_{cm,ak}}{2}S_{cm,ak}+\sum_{n}\frac{P_{cm,bn}}{2}S_{cm,ak}S_{bn,ak}\right)+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}$$

$$\left.\left.\times\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,ak}S_{dw,ak}-1\right\}(\alpha_{ak}-I_{ak,ak})\right] \quad ..(28)$$

Similarly expanding

$$\phi_{oj}=\sum_{t=1}^{\infty}S_{oj,bt}\phi_{bt}\,;\; o=a,c,d,\,;\; j=k,m,w,..(29)$$

and setting the overlap charge density $\phi_{bt}(i)\phi_{br}(i)=\delta_{tr}$, following the steps from (22) to (28) we got

$$H_{ak,bl} = S_{ak,bl}\left[\alpha_{bl}+\left\{\sum_{u}\frac{P_{bl,au}}{2}S_{au,bl}+\sum_{c\neq a,b}\sum_{m}\right.\right.$$

$$\left(\frac{P_{cm,bl}}{2}S_{cm,bl}+\sum_{u}\frac{P_{cm,au}}{2}S_{cm,bl}S_{au,bl}\right)+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}$$

$$\left.\left.\times\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,bl}S_{dw,bl}-1\right\}(\alpha_{bl}-I_{bl,bl})\right] \quad .(30)$$

where α_{bl} and $I_{bl,bl}$ are defined by (19), replacing the indices *a* and k with *b* and *l*.

Combining (28) and (30) for the $H_{ak,bl}$ integral, noting that from (9) $S_{ak,bl} = S_{bl,ak}$, we obtain the compact expression

$$H_{ak,bl} = K_{ak,bl}S_{ak,bl}\frac{(\alpha_{ak}+\alpha_{bl})}{2} \quad ....(31)$$

which has exactly the same form as the Wolfberg - Helmholz's empirical formula (2), except that in this case the parameter K is defined literarily explicitly by

$$K_{ak,bl} = 1+\left\{\sum_{n}\frac{P_{ak,bn}}{2}S_{bn,ak}+\sum_{c\neq a,b}\sum_{m}\left(\frac{P_{cm,ak}}{2}S_{cm,ak}+\sum_{n}\frac{P_{cm,bn}}{2}S_{cm,ak}S_{bn,ak}\right)+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}\right.$$

$$\times S_{cm,ak}S_{dw,ak} - 1\Big\}\frac{\alpha_{ak} + I_{ak,ak}}{\alpha_{ak} + \alpha_{bl}} + \Big\{\sum_{u}\frac{P_{bl,au}}{2}S_{au,bl} + \sum_{c\neq a,b}\sum_{m}\left(\frac{P_{cm,bl}}{2}S_{cm,bl} + \sum_{u}\frac{P_{cm,au}}{2}S_{cm,bl}S_{au,bl}\right)$$

$$+ \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}S_{cm,bl}S_{dw,bl} - 1\Big\}\frac{\alpha_{bl} + I_{bl,bl}}{\alpha_{ak} + \alpha_{bl}}$$

$$= 1 + \sigma_{ak,bl} \quad \text{..........(32)}$$

$\sigma_{ak,bl}$ is a function of bond orders, overlap - therefore intermolecular distance, and basis orbital energies. Hence K depends on both the nature of the individual moieties *a*, *b*, *c*, *d*, etc. and the extent of interaction between them. Since $\sigma_{ak,bl}$ depends upon the interaction between the moieties *a* and *b*, then it should identically vanish when they are at infinite separation away from one another. That is, it must converge to zero at the limit $R_{ab} \to 0$. Looking at the expression for $\sigma_{ak,bl}$ in (32), this condition is not satisfied. In the following section, the logical form of $\sigma_{ak,bl}$ that satisfies this convergence condition and its physical significance shall be discussed.

Determination of the bound $\sigma_{ak,bl}$ and its physical significance

We begin by writing the electronic energy of the molecule (for a closed shell system) as

$$E = 2\sum_{p}^{occupied}\varepsilon_p$$

$$= \sum_{a}\sum_{k}P_{ak,ak}H_{ak,ak} + \sum_{a}\sum_{k}\sum_{b}\sum_{l}P_{ak,bl}H_{ak,bl}$$

$$= \sum_{a}\sum_{k}P_{ak,ak}(1 + \omega_{ak})\alpha_{ak}$$

$$+ \sum_{a}\sum_{k}\sum_{b}\sum_{l}P_{ak,bl}(1 + \sigma_{ak,bl})S_{ak,bl}\frac{\alpha_{ak} + \alpha_{bl}}{2} \quad \text{.(33)}$$

using (7), (18), (31) and (32). Consider now the energy required to dissociate the molecule into widely separated moieties, ΔE. This is the binding energy of the molecule and is the second term of (33):

$$\Delta E = \sum_{a}\sum_{k}\sum_{b}\sum_{l}P_{ak,bl}(1 + \sigma_{ak,bl})S_{ak,bl}\frac{\alpha_{ak} + \alpha_{bl}}{2}$$

$$\text{..........(34)}$$

The sum consists of a number of terms, each referring to orbitals of one pair of moieties *a* and *b*.

When electron distribution in the {*a* - *b*} regions is zero all the *a*, *b*, *c*, *d*, ... moieties are separated, and the binding energy ΔE = 0. Identically all the $\{P_{ak,bl}, \sigma_{ak,bl}$ and $S_{ak,bl}\}$ quantities must vanish under this condition. This is the physical requirement that these quantities must satisfy. Fortunately, $\{P_{ak,bl}$ and $S_{ak,bl}\}$ have already met this condition; but $\sigma_{ak,bl}$ does not. Examining the expansion for $\sigma_{ak,bl}$ in (32) we found that, after some rearrangement, it may be casted as a sum of *convergent* and *divergent* terms:

$$\sigma_{ak,bl} = \Bigg[\sum_{n}\frac{P_{ak,bl}}{2}(S_{bn,ak} - 1) + \sum_{c\neq a,b}\sum_{m}\left\{\frac{P_{cm,ak}}{2}(S_{cm,ak} - 1) + \sum_{n}\frac{P_{cm,bn}}{2}(S_{cm,ak}S_{bn,ak} - 1)\right\}$$

$$+ \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}\frac{P_{cm,dw}}{2}(S_{cm,ak}S_{dw,ak} - 1)\Bigg]\frac{\alpha_{ak} - I_{ak,ak}}{\alpha_{ak} + \alpha_{bl}} + \Bigg[\sum_{u}\frac{P_{bl,au}}{2}(S_{au,bl} - 1) + \sum_{c\neq a,b}\sum_{m}\Bigg\{\frac{P_{cm,bl}}{2}$$

$$\times\ (S_{cm,bl} - 1) + \sum_{u} \frac{P_{cm,au}}{2}(S_{cm,bl}S_{au,bl} - 1)\Big\} + \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w} \frac{P_{cm,dw}}{2}(S_{cm,bl}S_{dw,bl} - 1)\Big] \frac{\alpha_{bl} - I_{bl,bl}}{\alpha_{ak} + \alpha_{bl}}$$

$$+ \text{ the divergent term} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(35)$$

Seeing that $\sigma_{ak,bl}$ must vanish in order to satisfy this physical requirement, then it reduces logically to the convergent term only in (35) - which has been written in full. That is, the divergent term should be cut off when calculating it.

In the expression for the bound $\sigma_{ak,bl}$, all the building blocks (or moieties) of the molecule interact with one another. In practice, most of the $\Sigma_{c\neq a,b}\Sigma_m$ and $\Sigma_{c\neq a,b}\Sigma_m\Sigma_{d\neq a,b}\Sigma_w$ terms may turn out to be zero, especially when topological approximations are invoked. In fact, the main contribution to it would be due to the

$$\sum_{n} \frac{P_{ak,bn}}{2}(S_{bn,ak} - 1)\frac{\alpha_{ak} - I_{ak,ak}}{\alpha_{ak} + \alpha_{bl}} + \sum_{u} \frac{P_{bl,au}}{2}$$

$$\times\ (S_{au,bl} - 1)\frac{\alpha_{bl} - I_{bl,bl}}{\alpha_{ak} + \alpha_{bl}} \qquad \ldots\ldots\ldots\ldots\ldots(36)$$

nearest neighbour terms. Whence, from the proceeding sections, it has been shown that the parameters *α, β, K, ω* of the Wheland and Mann's and Wolfberg - Helmholz's parametric expressions (1), (2) and (4) now have literal or theoretical basis and can all be calculated from first principles. The conclusion of *ab initio* theorists, that these semiempirical parameters are ill-founded, is then seen to result from an overly naive or literal interpretation of these theories.

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