ab initio EVALUATION OF THE α, β, K, ω PARAMETERS OF THE SEMIEMPIRICAL THEORIES II: SPIN - POLARIZED VERSION

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ABSTRACT
The derivation of the α, β, K, ω parameters of the Wolfberg - Helmholz's and Wheland & Mann's semiempirical theories is presented from first principles calculations for spin-polarized systems in their ground state. The notion of some ab initio theorists that these parameters cannot find any support in the non-empirical theory has been shown to be a naive interpretation of the semiempirical theories.

ab initio DERIVATION OF THE α, β, K, ω SEMIEMPIRICAL PARAMETERS: SPIN - POLARIZED CASE

In the first report[1] of this work we presented the interpretation of the α, β, K, ω parameters of the semiempirical theories of electronic structure calculations for a closed shell system in terms of *ab initio* theory. In the present article, the derivation of these parameters for the case of a general *open shell system* in which the ground state can be represented by a single determinant wavefunction is examined. For such a state we may associate M electrons with orthogonal orbitals $\psi_1^{\uparrow} .....\psi_M^{\uparrow}$ and ↑-spin functions and the remaining N electrons with orbitals $\psi_1^{\downarrow} .....\psi_N^{\downarrow}$ and ↓-spin functions. Furthermore, there is no *a priori* reason why any of the orbitals in one set should be identical with any in the other. Using the true Hamiltonian with one- and two-electron operators and the zeroth order spin-polarized determinant wavefunction, it has been shown[2] that the one-electron molecular orbitals $\{ \psi_p^{\uparrow} ; p = 1, 2, ..., M\}$ and $\{ \psi_p^{\downarrow} ; p = 1, 2, ..., N\}$ satisfy

$$H_i^{\uparrow}\psi_p^{\uparrow}(i) = \varepsilon_p^{\uparrow}\psi_p^{\uparrow}(i) \quad p = 1,2,......,M \quad ....(1)$$

and

$$H_i^{\downarrow}\psi_p^{\downarrow}(i) = \varepsilon_p^{\downarrow}\psi_p^{\downarrow}(i) \quad p = 1,2,......,N \quad ....(2)$$

equations, $H_i^{\uparrow}$ *and* $H_i^{\downarrow}$ being one-electron spin-polarized operators. The molecular orbitals may be expanded as linear combination of independent functions $\{ \phi_{au}, \phi_{bn}, \phi_{cm}, \phi_{dw} ; a, b, c, d, ...; u, n, m, w, ...\}$

$$\psi_p^{\uparrow} = \sum_a \sum_k C_{pak}^{\uparrow}\phi_{ak}, \quad ....(3)$$

with similar expression for $\psi_p^{\downarrow}$. Using (3), the trial one-electron energies become

$$\varepsilon_p^{\uparrow} = \sum_a \sum_k \sum_b \sum_l C_{pak}^{*\uparrow}C_{pbl}^{\uparrow}H_{ak,bl}^{\uparrow} / \sum_a \sum_k \sum_b \sum_l \times C_{pak}^{*\uparrow}C_{pbl}^{\uparrow}S_{ak,bl} \quad ....(4)$$

and

$$\varepsilon_p^{\downarrow} = \sum_a \sum_k \sum_b \sum_l C_{pak}^{*\downarrow}C_{pbl}^{\downarrow}H_{ak,bl}^{\downarrow} / \sum_a \sum_k \sum_b \sum_l \times C_{pak}^{*\downarrow}C_{pbl}^{\downarrow}S_{ak,bl} \quad ....(5)$$

From (4) and (5) it is an easy matter to show that the values of $C_{pak}^{*\uparrow}$ *and* $C_{pak}^{*\downarrow}$ which give the lowest values for the $\varepsilon_p^{\uparrow}$ *and* $\varepsilon_p^{\downarrow}$, respectively, and therefore the best approximation to the total energy,

$$E = \sum_p^{\uparrow} \varepsilon_p^{\uparrow} + \sum_p^{\downarrow} \varepsilon_p^{\downarrow},$$

satisfy

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$$\sum_b \sum_l C^{\uparrow}_{pbl}(H^{\uparrow}_{ak,bl} - \varepsilon^{\uparrow}_p S_{ak,bl}) = 0 \quad \ldots\ldots\ldots$$

$$\sum_b \sum_l C^{\downarrow}_{pbl}(H^{\downarrow}_{ak,bl} - \varepsilon^{\downarrow}_p S_{ak,bl}) = 0 \quad \ldots\ldots\ldots$$

for each a and k index as a condition for minimum. The $S_{ak,bl}$, $H^{\uparrow}_{ak,bl}$ *and* $H^{\downarrow}_{ak,bl}$ are defined as

$$S_{ak,bl} = \int \phi^*_{ak}\phi_{bl}d\tau \, , \qquad \ldots\ldots\ldots(8)$$

$$H^{\uparrow}_{ak,bl} = \left< \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{al}} \right| \phi_{bl} \right> + \sum_c \sum_m \sum_d \sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(<\phi_{ak}\phi_{bl}|\phi_{cm}\phi_{dw}>$$
$$- \eta^{\uparrow} <\phi_{ak}\phi_{cm}|\phi_{bl}\phi_{dw}>) \qquad \ldots\ldots\ldots(9)$$

and

$$H^{\downarrow}_{ak,bl} = \left< \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{al}} \right| \phi_{bl} \right> + \sum_c \sum_m \sum_d \sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(<\phi_{ak}\phi_{bl}|\phi_{cm}\phi_{dw}>$$
$$- \eta^{\downarrow} <\phi_{ak}\phi_{cm}|\phi_{bl}\phi_{dw}>) \qquad \ldots\ldots\ldots(10)$$

where

$$P^{\uparrow}_{cm,dw} = \sum_q^{\uparrow} C^{*\uparrow}_{qcm} C^{\uparrow}_{qdw}, \; P^{\downarrow}_{cm,dw} = \sum_q^{\downarrow} C^{*\downarrow}_{qcm} C^{\downarrow}_{qdw}, \; \eta^{\uparrow} = \frac{P^{\uparrow}_{cm,dw}}{(P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})} \; and \; \eta^{\downarrow} = \frac{P^{\downarrow}_{cm,dw}}{(P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})}$$
$$\ldots\ldots\ldots(11)$$

Equations (9) and (10) are our starting points.

Evaluation of the spin-polarized Wheland & Mann's parameters α and ω

The $H^{\uparrow}_{ak,ak}$ spin-polarized diagonal matrix element, i.e. the case a = b and k = l in (9), are

$$H^{\uparrow}_{ak,ak} = \left< \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{al}} \right| \phi_{ak} \right> + \sum_c \sum_m \sum_d \sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(<\phi_{ak}\phi_{ak}|\phi_{cm}\phi_{dw}>$$
$$- \eta^{\uparrow} <\phi_{ak}\phi_{cm}|\phi_{ak}\phi_{dw}>)$$
$$= \left< \phi_{ak} \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{al}} \right| \phi_{ak} \right> + \sum_u (P^{\uparrow}_{au,au} + P^{\downarrow}_{au,au})(<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}>$$
$$- \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>) + \sum_u \sum_{c\neq a} \sum_m (P^{\uparrow}_{cm,au} + P^{\downarrow}_{cm,au})(<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{cm}>$$
$$- \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{cm}>) + \sum_{c\neq a} \sum_m \sum_{d\neq a} \sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(<\phi_{ak}\phi_{ak}|\phi_{cm}\phi_{dw}>$$
$$- \eta^{\uparrow} <\phi_{ak}\phi_{cm}|\phi_{ak}\phi_{dw}>) \qquad \ldots\ldots\ldots(12)$$

To transform the two- and multi-center integrals to one-center integrals, we use the Ruedenberg's approximation[3]. That is

$$\phi_{oj} = \sum_{r=1}^{\infty} S_{oj,or}\phi_{or}; \quad o = a,b,c,d,\ldots\ldots; \; j = k,l,m,w,\ldots\ldots\ldots\ldots \qquad \ldots\ldots\ldots\ldots(13)$$

Setting the overlap charge density $\phi_{at}\phi_{ar} = \delta_{tr}$ and putting (13) in (12), we obtain

$$H^{\uparrow}_{ak,ak} = <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{ai}}\right|\phi_{ak}> + \sum_u (<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}> - \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>)$$

$$+ \{(P^{\uparrow}_{ak,ak} + P^{\downarrow}_{ak,ak}) + \sum_{c\neq a}\sum_m (P^{\uparrow}_{cm,ak} + P^{\downarrow}_{cm,ak})S_{cm,ak} + \sum_{c\neq a}\sum_m\sum_{d\neq a}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})$$

$$\times S_{cm,ak}S_{dw,ak} - 1\}\sum_u (<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}> - \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>)$$

$$= (1 + \omega^{\uparrow}_{ak})\alpha^{\uparrow}_{ak} \qquad \ldots\ldots\ldots\ldots(14)$$

by adding

$$\sum_u (<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}> - \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>) \qquad \ldots\ldots\ldots\ldots(15)$$

to (12) and subtracting same from it, and letting

$$(P^{\uparrow}_{au,au} + P^{\downarrow}_{au,au}) + \sum_{c\neq a}\sum_m (P^{\uparrow}_{cm,au} + P^{\downarrow}_{cm,au})S_{cm,au} + \sum_{c\neq a}\sum_m\sum_{d\neq a}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})S_{cm,au}S_{dw,au} - 1$$

$$\cong$$

$$(P^{\uparrow}_{ak,ak} + P^{\downarrow}_{ak,ak}) + \sum_{c\neq a}\sum_m (P^{\uparrow}_{cm,ak} + P^{\downarrow}_{cm,ak})S_{cm,ak} + \sum_{c\neq a}\sum_m\sum_{d\neq a}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})S_{cm,ak}S_{dw,ak} - 1 \ldots(16)$$

all u index. The $\alpha^{\uparrow}_{ak}$'s, which depend on the nature of the *a*th moiety only, are defined as

$$\alpha^{\uparrow}_{ak} = <\phi_{ak}\left|-\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{ai}}\right|\phi_{ak}> + \sum_u (<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}> - \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>)$$

$$= I_{ak,ak} + \sum_u (<\phi_{ak}\phi_{ak}|\phi_{au}\phi_{au}> - \eta^{\uparrow} <\phi_{ak}\phi_{au}|\phi_{ak}\phi_{au}>) \qquad \ldots\ldots\ldots\ldots(17)$$

The $\omega^{\uparrow}_{ak}$ parameter is also defined as

$$\omega^{\uparrow}_{ak} = \{(P^{\uparrow}_{ak,ak} + P^{\downarrow}_{ak,ak}) + \sum_{c\neq a}\sum_m (P^{\uparrow}_{cm,ak} + P^{\downarrow}_{cm,ak})S_{cm,ak} + \sum_{c\neq a}\sum_m\sum_{d\neq a}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})$$

$$\times S_{cm,ak}S_{dw,ak} - 1\}\frac{\alpha^{\uparrow}_{ak} - I_{ak,ak}}{\alpha^{\uparrow}_{ak}} \qquad \ldots\ldots\ldots\ldots(18)$$

Following the same procedure for $H^{\downarrow}_{ak,ak}$ from equation (12) to (16), we got

$$H^{\downarrow}_{ak,ak} = (1 + \omega^{\downarrow}_{ak})\alpha^{\downarrow}_{ak} \qquad \ldots\ldots\ldots\ldots(19)$$

where

$$\alpha_{ak}^{\downarrow} = I_{ak,ak} + \sum_{u} (< \phi_{ak}\phi_{ak} | \phi_{au}\phi_{au} > - \eta^{\downarrow} < \phi_{ak}\phi_{au} | \phi_{ak}\phi_{au} >) \quad \text{......(20)}$$

and

$$\omega_{ak}^{\downarrow} = \{(P_{ak,ak}^{\uparrow} + P_{ak,ak}^{\downarrow}) + \sum_{c\neq a}\sum_{m} (P_{cm,ak}^{\uparrow} + P_{cm,ak}^{\downarrow})S_{cm,ak} + \sum_{c\neq a}\sum_{m}\sum_{d\neq a}\sum_{w} (P_{cm,dw}^{\uparrow} + P_{cm,dw}^{\downarrow})$$

$$\times S_{cm,ak}S_{dw,ak} - 1\} \frac{\alpha_{ak}^{\downarrow} - I_{ak,ak}}{\alpha_{ak}^{\downarrow}} \quad \text{......(21)}$$

As could be seen from (18) and (21), both $\omega_{ak}^{\uparrow}$ *and* $\omega_{ak}^{\downarrow}$ parameters are functions of charges, bond orders, overlap and basis orbital energies. Because $\alpha_{ak}^{\uparrow} \neq \alpha_{ak}^{\downarrow}$ for spin-polarized or open shell systems, $\omega_{ak}^{\uparrow} \neq \omega_{ak}^{\downarrow}$. In addition, they have no spin-polarized semiempirical counterparts. However, the main contribution to these parameters come from $(P_{ak,ak}^{\uparrow} + P_{ak,ak}^{\downarrow} - 1)$ terms in (18) and (21) which account for charge deflation on the ath moiety due to an electron in ϕ_{ak} - exactly as in the Wheland & Mann's semiempirical approximation[4]. Moreover, the third and most of the second terms in these equations vanish if only nearest neighbour interactions are allowed.

Evaluation of the spin-polarized Wolfberg - Helmholz parameters β and K

The $H_{ak,bl}^{\uparrow}$ spin-polarized off-diagonal matrix elements are given by (9). Now, making use of (13) and (15) in this equation, we obtain

$$H_{ak,bl}^{\uparrow} = S_{bl,ak}[\alpha_{ak}^{\uparrow} + \{\sum_{n} (P_{ak,bn}^{\uparrow} + P_{ak,bn}^{\downarrow})S_{bn,ak} + \sum_{c\neq a,b}\sum_{m} ((P_{cm,ak}^{\uparrow} + P_{cm,ak}^{\downarrow})S_{cm,ak}$$

$$+ \sum_{n} (P_{cm,bn}^{\uparrow} + P_{cm,bn}^{\downarrow})S_{cm,ak}S_{bn,ak}) + \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w} (P_{cm,dw}^{\uparrow} + P_{cm,dw}^{\downarrow})S_{cm,ak}S_{dw,ak} - 1\}$$

$$\times (\alpha_{ak}^{\uparrow} - I_{ak,ak})] \quad \text{......(22)}$$

and

$$H_{ak,bl}^{\uparrow} = S_{ak,bl}[\alpha_{bl}^{\uparrow} + \{\sum_{u} (P_{bl,au}^{\uparrow} + P_{bl,au}^{\downarrow})S_{au,bl} + \sum_{c\neq a,b}\sum_{m} ((P_{cm,bl}^{\uparrow} + P_{cm,bl}^{\downarrow})S_{cm,bl}$$

$$+ \sum_{u} (P_{cm,au}^{\uparrow} + P_{cm,au}^{\downarrow})S_{cm,bl}S_{au,bl}) + \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w} (P_{cm,dw}^{\uparrow} + P_{cm,dw}^{\downarrow})S_{cm,bl}S_{dw,bl} - 1\}$$

$$\times (\alpha_{bl}^{\uparrow} - I_{bl,bl})] \quad \text{......(23)}$$

respectively, invoking the

$$(i) \sum_{n} (P_{au,bn}^{\uparrow} + P_{au,bn}^{\downarrow})S_{bn,au} \cong \sum_{n} (P_{ak,bn}^{\uparrow} + P_{au,bn}^{\downarrow})S_{bn,ak} \quad \text{......(24)}$$

$$(ii) \sum_{c\neq a,b}\sum_{m} \{(P_{cm,au}^{\uparrow} + P_{cm,au}^{\downarrow})S_{cm,au} + \sum_{n} (P_{cm,bn}^{\uparrow} + P_{cm,bn}^{\downarrow})S_{cm,au}S_{bn,au}$$

$$\cong \sum_{c\neq a,b}\sum_{m} \{(P_{cm,ak}^{\uparrow} + P_{cm,ak}^{\downarrow})S_{cm,ak} + \sum_{n} (P_{cm,bn}^{\uparrow} + P_{cm,bn}^{\downarrow})S_{cm,ak}S_{bn,ak}$$

and

$$(iii)\ \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}(P^{\uparrow}_{cm,dw}+P^{\downarrow}_{cm,dw})S_{cm,au}S_{dw,au}$$

$$\cong \sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}(P^{\uparrow}_{cm,dw}+P^{\downarrow}_{cm,dw})S_{cm,ak}S_{dw,ak} \qquad (25)$$

approximation. Combining (22) and (23), noting that $S_{ak,bl} = S_{bl,ak}$, we have the compact expression

$$H^{\uparrow}_{ak,bl} = K^{\uparrow}_{ak,bl}S_{ak,bl}\frac{\alpha^{\uparrow}_{ak}+\alpha^{\uparrow}_{bl}}{2} \qquad (26)$$

which has exactly the same form as the Wolfberg - Helmholz's empirical formula[5], where

$$K^{\uparrow}_{ak,bl} = 1+\{\sum_{n}(P^{\uparrow}_{ak,bn}+P^{\downarrow}_{ak,bn})S_{bn,ak}+\sum_{c\neq a,b}\sum_{m}((P^{\uparrow}_{cm,ak}+P^{\downarrow}_{cm,ak})S_{cm,ak}+\sum_{n}(P^{\uparrow}_{cm,bn}+P^{\downarrow}_{cm,bn})$$

$$\times S_{cm,ak}S_{bn,ak})+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}(P^{\uparrow}_{cm,dw}+P^{\downarrow}_{cm,dw})S_{cm,ak}S_{dw,ak}-1\}\frac{\alpha^{\uparrow}_{ak}-I_{ak,ak}}{\alpha^{\uparrow}_{ak}+\alpha^{\uparrow}_{bl}}+\{\sum_{u}(P^{\uparrow}_{bl,au}+P^{\downarrow}_{bl,au})$$

$$\times S_{au,bl}+\sum_{c\neq a,b}\sum_{m}((P^{\uparrow}_{cm,bl}+P^{\downarrow}_{cm,bl})S_{cm,bl}+\sum_{u}(P^{\uparrow}_{cm,au}+P^{\downarrow}_{cm,au})S_{cm,bl}S_{au,bl})+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}$$

$$\times S_{cm,bl}S_{dw,bl}-1\}\frac{\alpha^{\uparrow}_{bl}-I_{bl,bl}}{\alpha^{\uparrow}_{ak}+\alpha^{\uparrow}_{bl}}$$

$$=(1+\sigma^{\uparrow}_{ak,bl}) \qquad (27)$$

In the same way, we obtain

$$H^{\downarrow}_{ak,bl} = K^{\downarrow}_{ak,bl}S_{ak,bl}\frac{\alpha^{\downarrow}_{ak}+\alpha^{\downarrow}_{bl}}{2} \qquad (28)$$

where

$$K^{\downarrow}_{ak,bl} = 1+\{\sum_{n}(P^{\uparrow}_{ak,bn}+P^{\downarrow}_{ak,bn})S_{bn,ak}+\sum_{c\neq a,b}\sum_{m}((P^{\uparrow}_{cm,ak}+P^{\downarrow}_{cm,ak})S_{cm,ak}+\sum_{n}(P^{\uparrow}_{cm,bn}+P^{\downarrow}_{cm,bn})$$

$$\times S_{cm,ak}S_{bn,ak})+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}(P^{\uparrow}_{cm,dw}+P^{\downarrow}_{cm,dw})S_{cm,ak}S_{dw,ak}-1\}\frac{\alpha^{\downarrow}_{ak}-I_{ak,ak}}{\alpha^{\downarrow}_{ak}+\alpha^{\downarrow}_{bl}}+\{\sum_{u}(P^{\uparrow}_{bl,au}+P^{\downarrow}_{bl,au})$$

$$\times S_{au,bl}+\sum_{c\neq a,b}\sum_{m}((P^{\uparrow}_{cm,bl}+P^{\downarrow}_{cm,bl})S_{cm,bl}+\sum_{u}(P^{\uparrow}_{cm,au}+P^{\downarrow}_{cm,au})S_{cm,bl}S_{au,bl})+\sum_{c\neq a,b}\sum_{m}\sum_{d\neq a,b}\sum_{w}$$

$$\times S_{cm,bl}S_{dw,bl}-1\}\frac{\alpha^{\downarrow}_{bl}-I_{bl,bl}}{\alpha^{\downarrow}_{ak}+\alpha^{\downarrow}_{bl}}$$

$$=(1+\sigma^{\downarrow}_{ak,bl}) \qquad (29)$$

Equation (26) and (28) have exactly the same form as the Wolfberg - Helmholz empirical formula[5], save that $K^{\uparrow}_{ak,bl}$ *and* $K^{\downarrow}_{ak,bl}$ have no semiempirical counterparts. Again, because $\{\alpha^{\uparrow}_{ak},\ \alpha^{\uparrow}_{bl}\}\neq\{\alpha^{\downarrow}_{ak},\ \alpha^{\downarrow}_{bl}\}$

for a spin-polarized system, $K^{\uparrow}_{ak,bl} \neq K^{\downarrow}_{ak,bl}$.

Calculation of the $K^{\uparrow}_{ak,bl}$ and $K^{\downarrow}_{ak,bl}$ parameters

The binding energy, ΔE, of the spin-polarized system is given by

$$\Delta E = \sum_a \sum_k \sum_b \sum_l P^{\uparrow}_{ak,bl}(1+\sigma^{\uparrow}_{ak,bl})S_{ak,bl}\frac{\alpha^{\uparrow}_{ak}+\alpha^{\uparrow}_{bl}}{2} + \sum_a \sum_k \sum_b \sum_l P^{\downarrow}_{ak,bl}(1+\sigma^{\downarrow}_{ak,bl})S_{ak,bl}\frac{\alpha^{\downarrow}_{ak}+\alpha^{\downarrow}_{bl}}{2} \quad \text{.......(30)}$$

When all the *a*, *b*, ...moieties are widely separated entities, the binding energy ΔE = 0. Now, since $\{P^{\uparrow}_{ak,bl}, P^{\downarrow}_{ak,bl}, \sigma^{\uparrow}_{ak,bl}, \sigma^{\downarrow}_{ak,bl}, S_{ak,bl}\}$ quantities depend upon the interaction between the moieties *a* and b they must also vanish in the limit $R_{ab} \to \infty$. Only $\{\sigma^{\uparrow}_{ak,bl}, \sigma^{\downarrow}_{ak,bl}\}$ parameters do not, however, *converge* at this limit. Examining the expression (27) and rearranging it, we cast $\sigma^{\uparrow}_{ak,bl}$ as a sum of *convergent* and *divergent* terms:

$$\sigma^{\uparrow}_{ak,bl} = [\sum_n (P^{\uparrow}_{ak,bn} + P^{\downarrow}_{ak,bn})(S_{bn,ak} - 1) + \sum_{c\neq a,b}\sum_m \{(P^{\uparrow}_{cm,ak} + P^{\downarrow}_{cm,ak})(S_{cm,ak} - 1) + \sum_n (P^{\uparrow}_{cm,bn} + P^{\downarrow}_{cm,bn})$$

$$\times (S_{cm,ak}S_{bn,ak} - 1)\} + \sum_{c\neq a,b}\sum_m \sum_{d\neq a,b}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(S_{cm,ak}S_{dw,ak} - 1)]\frac{\alpha^{\uparrow}_{ak} - I_{ak,ak}}{\alpha^{\uparrow}_{ak} + \alpha^{\uparrow}_{bl}}$$

$$+ [\sum_u (P^{\uparrow}_{bl,au} + P^{\downarrow}_{bl,au})(S_{au,bl} - 1) + \sum_{c\neq a,b}\sum_m \{(P^{\uparrow}_{cm,bl} + P^{\downarrow}_{cm,bl})(S_{cm,bl} - 1) + \sum_u (P^{\uparrow}_{cm,au} + P^{\downarrow}_{cm,au})$$

$$\times (S_{cm,bl}S_{au,bl} - 1)\} + \sum_{c\neq a,b}\sum_m \sum_{d\neq a,b}\sum_w (P^{\uparrow}_{cm,dw} + P^{\downarrow}_{cm,dw})(S_{cm,bl}S_{dw,bl} - 1)]\frac{\alpha^{\uparrow}_{bl} - I_{bl,bl}}{\alpha^{\uparrow}_{ak} + \alpha^{\uparrow}_{bl}}$$

$$+ \textit{the divergent term} \quad \text{.......(31)}$$

with similar expression for $\sigma^{\downarrow}_{ak,bl}$, replacing $\{\alpha^{\uparrow}_{ak}, \alpha^{\uparrow}_{bl}\}$ with $\{\alpha^{\downarrow}_{ak}, \alpha^{\downarrow}_{bl}\}$ Since $\{\sigma^{\uparrow}_{ak,bl}, \sigma^{\downarrow}_{ak,bl}\}$ must vanish in the limit $R_{ab} \to \infty$, the divergent term should then be cut off from (31). However, most of the $\Sigma_{c\neq a,b}\Sigma_m$ and $\Sigma_{c\neq a,b}\Sigma_m\Sigma_{d\neq a,b}\Sigma_w$ contributions may actually turn out to be zero, especially when topological approximations are used.

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