A Semi-empirical MO Theory of σ Electron Systems. III. The Bond Additivity Rule*

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We have already established[1,2] that σ electron systems may usually be regarded as consisting of localized electron pairs, and that our first order theory corresponds to the localized bond model. This idea seems to be supported by the fact that many molecular quantities, such as heats of formation, dipole moments, and polarizabilities,[3] may be derived by means of bond additivity rules. At first sight, therefore, the empirical additivity rules seem to be based essentially on the localization of σ electrons. However, we have shown[2] in the first order theory how same bonds may vary in different molecules because of changes in the bond polarity which are due to the inductive effect. This suggests that the different bond quantities may be assigned to the bonds in different molecules and that the additivity rules do not necessarily hold.

On the other hand, some deviations from the additivity of bond properties due to the delocalization effects have been found. This has been accounted for in our theory as the second order approximation.[1] In spite of these facts, it appears that the empirical rules reveal a much more exact additivity of all the bond properties than should be expected. This problem for the additivity of bond energies has been discussed by several authors[4-7] using different approaches, but the additivity of bond moments in only a few molecules has been discussed.[8,9] We wish to discuss the additivity of bond energies and bond moments in general in this paper, including our second order theory, especially by taking the influence of the inductive effect into consideration.

I. The Bond Additivity of the Heat of Formation.—By making use of previous results[1] of the first and second order theory, we obtain the heats of the formation of molecules:

$$W=\sum_{\mathrm{p}}\overline{W}_{\mathrm{p}}^{-2}\sum_{\mathrm{ik}}(\beta_{\mathrm{ik}}^{+-})^2/(\varepsilon_{\mathrm{k}}^{-}-\varepsilon_{\mathrm{i}}^{+})+1/2\sum_{\mathrm{1m}}Z_1'Z_{\mathrm{m}}'/R_{\mathrm{1m}}-\sum_{a}W_{\mathrm{a}}^{\circ} \tag{1}$$

where $\overline{W}_{\mathrm{p}}$ is the bond energy for each orthogonalized BO defined by Eq. 14 of Ref. 1; the second term is a resonance energy in terms of our second order theory; Z_1' and Z_{m}' denote the effective nuclear charges of the atoms 1 and m including the inner shell electrons, respectively; R_{1m} is the internuclear distance, and W_{a}° is the energy of the atom a at infinite separation, excluding the energy of the inner-shell electrons. The third term, which corresponds to the internuclear repulsion energy including inner-shell electrons, may be rewritten as:

$$\sum_{\mathrm{1m}}Z_1'Z_{\mathrm{m}}'/R_{\mathrm{1m}}=\sum_{\mathrm{ab}}Z_{\mathrm{a}}'Z_{\mathrm{b}}'/R_{\mathrm{ab}}+\sum_{\mathrm{cd}}Z_{\mathrm{c}}'Z_{\mathrm{d}}'/R_{\mathrm{cd}} \tag{2}$$

where the a and b denote the directly-bonded atoms, and the c and d, the other pairs. The $\sum\overline{W}_{\mathrm{p}}$ may be expanded as a power series in S_{pq}:[10]

$$\sum_{\mathrm{p}}\overline{W}_{\mathrm{p}}=\sum_{\mathrm{p}}W_{\mathrm{pp}}-\sum_{\substack{\mathrm{pq}\\(\mathrm{q}\neq\mathrm{p})}}S_{\mathrm{pq}}W_{\mathrm{pq}}+\cdots\cdots \tag{3}$$

where

$$W_{\mathrm{pq}}=2H_{\mathrm{pq}}+(2-\delta_{\mathrm{pq}})\sum_{\mathrm{r}}[2\langle\varphi_{\mathrm{r}}(1)\varphi_{\mathrm{p}}(2)\cdot|\boldsymbol{r}_{12}^{-1}|\,\varphi_{\mathrm{r}}(1)\varphi_{\mathrm{q}}(2)\rangle-\langle\varphi_{\mathrm{r}}(1)\varphi_{\mathrm{p}}(2)\cdot|\boldsymbol{r}_{12}^{-1}|\,\varphi_{\mathrm{q}}(1)\varphi_{\mathrm{r}}(2)\rangle]\quad\text{etc.}$$

Since, in general, the overlap integrals, S_{pq}, between different BO are much smaller than the integrals, S_{p}, between directly-bonded

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1) The first paper of this series. This Bulletin, 37. 1574 (1964).

2) The second paper of this series. ibid., 37, 1583 (1964).

3) K. G. Denbigh, *Trans. Faraday Soc.*, 36, 936 (1940).

4) R. D. Brown, *J. Chem. Soc.*, 1953, 2615.

5) G. G. Hall, *Proc. Roy. Soc.*, A213, 113 (1952).

6) J. M. Parks and R. G. Parr, *J. Chem. Phys.*, 28, 335 (1958).

7) T. L. Allen and H. Shull, ibid., 35, 1644 (1961).

8) C. A. Coulson, *Trans. Faraday Soc.*, 38, 433 (1942); 33, 388 (1937).

9) W. C. Hamilton, *J. Chem. Phys.*, 26, 345 (1957).

10) Here the expansion $(1+S^{\circ})_{\mathrm{pq}}^{-1/2}=\delta_{\mathrm{pp}}-1/2S_{\mathrm{pq}}+3/8\sum_{\mathrm{r}}S_{\mathrm{pr}}S_{\mathrm{rq}}\cdots$ is used. See also Eqs. 9 and 10 of Ref. 1.

orbitals, only terms containing zeroth and first powers of S_{pq} in Eq. 3 may be considered. The first term, W_{pp}, may be regarded as the energy of the pth bond or lone pair; the sum is equivalent to the W_e° given by Eq. 17 or 20 of Ref. 1, whereas the second term, W_{pq}, is connected with the interaction energy between different bonds or lone pairs.

First let us examine the quantity W_e°. Since the discussion of the bond additivity may be restricted to the case of bonds with small polarities, we may use the approximation $F_p \sim (1+S_p)^{-1} - 1/2Q_p^2$.[1] Thus we obtain for W_e°:

$$W_e^\circ = \sum_a (W_a + W_a') + \sum_p{}' (E_p + \Delta_p) \tag{4}$$

where

$$\begin{aligned} W_a = & \sum_{R,\,p(a)} H^\circ_{R,p(a)} + 2\sum_{f(a)} H^\circ_{f(a)} + \\ & 1/2 \sum_{\substack{R,\,p(a)\,T,\,q(a)\\(q\neq p)}} (J^\circ_{R,p(a)T,q(a)} - 1/2K^\circ_{R,p(a)T,q(a)}) \\ & + 2\sum_{f(a)R,p(a)} (J^\circ_{f(a)R,p(a)} - 1/2K^\circ_{f(a)R,p(a)}) \\ & + 2\sum_{f(a)g(a)} (J^\circ_{f(a)g(a)} - 1/2K^\circ_{f(a)g(a)}) \end{aligned} \tag{5}$$

$$\begin{aligned} W_a' = & \sum_{R,p(a)} H''_{R,p(a)} + 2\sum_{f(a)} H''_{f(a)} + 1/2 \\ & \sum_{\substack{R,p(a)T,q\\(q\neq p)}} J''_{R,p(a)T,q} + \sum_{f(a)R,p} J''_{f,(a)R,p} \\ & + \sum_{R,p(a)f} J''_{R,p(a)f} + 2\sum_{f(a)g} J''_{f(a)g} \end{aligned} \tag{6}$$

$$\begin{aligned} E_p = & (H^*_{A,p} + H^*_{B,p}) + 2(\sum_{f(A)} H^*_{f(A)} + \sum_{f(B)} H^*_{f(B)}) \\ & + 1/4(J^\circ_{A,pA,p} + J^\circ_{B,pB,p}) + 1/2(\sum_{\substack{B,q\\(q\neq p)}} J^*_{A,pB,q} \\ & + \sum_{A,q} J^*_{B,pA,q}) + 2(\sum_{f(B)} J^*_{A,pf(B)} + \sum_{f(A)} J^*_{B,pf(A)}) \\ & + 4\sum_{f(A)g(B)} J^*_{f(A)g(B)} + 1/2J^*_{A,pB,p} + 2\gamma_p(1+S_p)^{-1} \end{aligned} \tag{7}$$

$$\begin{aligned} \Delta_p = & \overline{Q}_p^2\ [1/4(J_{A,pA,p} + J_{B,pB,p}) - 1/2J^*_{A,pB,p} \\ & - \gamma_p] + \overline{Q}_p [(H_{B,p} - H_{A,p}) + 1/2(J_{B,pB,p} \\ & - J_{A,pA.p}) + \sum_{\substack{T,\,q\\(q\neq p)}} (1 - \overline{Q}_q^T)\{(J_{B,pT,q} \\ & - 1/2\delta_{B,pT,q}K_{B,pT,q}) - (J_{A,pT,q} - \\ & 1/2\delta_{A,pT,q}K_{A,pT,q})\} + 2\sum_f \{(J_{fB,p} - \\ & 1/2\delta_{fB,p}K_{fB,p}) - (J_{fA,p} - 1/2\delta_{fA,p}K_{fA,p})\}] \end{aligned} \tag{8}$$

and where $\sum_a$ and $\sum_p{}'$ denote summations over all atoms and over all bonds except lone pairs respectively; the parenthesis, (a), etc., of the AO refer to the atom, a etc., and the R, p, etc., stand for the valence AO A, p, B, p etc. The superscripts, small circle, asterisk and double prime of H, J., etc., denote the one-center integrals, two-center integrals between directly-bonded atoms and two-center integrals between the other paired atoms respectively under the conditions $H = H^\circ + H^* + H''$, etc. The symbol W_a represents the valence state energy of the atom a: the E_p and Δ_p correspond to the covalent bond energy and the ionic-covalent resonance energy of the bond p respectively. By using Eqs. 2, 3 and 4, Eq. 1 may be reduced to

$$\begin{aligned} W = & \sum_a \Delta W_a + [\sum_p{}' (E_p + \Delta_p) + 1/2\sum_{ab} Z_a' Z_b' / R_{ab}] \\ & + (\sum_a W_a' + 1/2\sum_{cd} Z_c' Z_d' / R_{cd}) - \sum_{\substack{pq\\(q\neq p)}} S_{pq} W_{pq} \\ & - 2\sum_{ik} (\beta_{ik}^{+-})^2 / (\varepsilon_k^- - \varepsilon_i^+) \end{aligned} \tag{9}$$

where $\Delta W_a (= W_a - W_a^\circ)$ is the promotion energy of the atom a. If there are n_a bonds connected with the atom a, then its contribution to the bond energy for each bond separately may be estimated as $\Delta W_a / n_a$, because the empirical bond energy contains implicitly the energy of lone pairs and all hybridized AO are here considered to be equivalent to each other. As can be seen from Eq. 6, the third term of Eq. 9 may be approximated as

$$\sum_a W_a' + 1/2\sum_{cd} Z_c' Z_d' / R_{cd} \sim 0 \tag{10}$$

The fourth and fifth terms of Eq. 9 are related to interaction energies between different bonds or lone pairs; although actually they may not be assigned to specific bonds or lone pairs, nevertheless it is possible[11] to do this in a strictly formal sense. Since usually $S_{pq} > 0$ and $W_{pq} < 0$, the fourth and fifth terms may be taken to be positive and negative respectively. It follows that the two terms tend to cancel each other and that the contribution of these terms to the bond energies is small.

Let us now consider the influence of the inductive effect on the heats of formation.

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[11] The fourth term may be assigned to specific bonds or lone pairs as follows from Eq. 3. It was shown by Dewar and Pettit (M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, **1954**, 1625) that if all bond orbitals are degenerated or almost degenerated the fifth term may be approximated by

$$\sum_{ik} (\beta_{ik}{}^{+-})^2 / (\varepsilon_k{}^- - \varepsilon_i{}^+) \sim \sum_{\substack{pq\\(p\neq q)}} (\beta_{pq}{}^{+-})^2 / (\varepsilon_q{}^- - \varepsilon_p{}^+)$$

where the p and q stand for bonding and antibonding orbitals respectively.

By using the results of Ref. 1, the Δ_p may be rewritten as:

$$\begin{aligned}\Delta_p &= -1/2\,K_p^{-1}\overline{Q}_p^2\\ &= -1/2K_p^{-1}[\overline{\Pi}_{pp}Q_p^{\circ 2}+2\overline{\Pi}_{pp}Q_p^{\circ}\sum_{q\neq p}\overline{\Pi}_{pq}Q_q^{\circ}\\ &\quad +(\sum_{q\neq p}\overline{\Pi}_{pq}Q_q^{\circ})^2]\end{aligned} \tag{11}$$

The second and third terms correspond to the induced energy at the bond p, they are generally small compared with the first term, because the quantities Q° and $\overline{\Pi}_{pq}$ ($p \neq q$) are smaller than unity and $\overline{\Pi}_{pp}$ is nearly equal to unity here.[1,2] For an essentially covalent bond ($Q_p^{\circ}=0$), the third term is important, but it is still small. It follows that the influence of the inductive effect on resonance energies is insignificant. Equation 11 also shows that the Δ_p values are negative and that their absolute values increase with an increase in the bond polarity; this has already been included in Pauling's theory.[12]

It may be difficult to predict the influence of the inductive effect on the fourth and fifth terms of Eq. 9; however, it can be inferred as follows: Electron transfer by the inductive effect occurs, as in Fig. 1 of Ref. 1, so that the induced energy in the term $S_{pq}W_{pq}$ tends to be cancelled and the induced energies in the paired quantities, $(\beta_{pq}^{+-})^2$ and $(\beta_{qp}^{+-})^2$, which appear in the quantities $(\beta_{ik}^{+-})^2$ also tend to cancel each other.[13] It seems, therefore, that the influence of the inductive effect on the heat of formation is very small. For example, in the series CH_3X, CH_2X_2, CHX_3 and CX_4 ($X=Cl$, Br, I), by taking the CH bond energies to be 90.4 kcal./mol.,[14] the C–Cl bond energies are empirically obtained as 71, 70, 70 and 69.6 kcal./mol.,[14] the C–Br bond energies, as 57, 57, 58 and 58 kcal./mol.,[14] and the C–I bond energies, as 43, 43 and 43 kcal./mol.[14] respectively. As has been shown in Ref. 2, however, the polarities of the CX bonds in these series are all changed by the inductive effect. Nevertheless, these bond energies and also the CH bond energies appear to be almost constant. This seems to confirm our inference. The bond energy, D_p, of the bond p, therefore, may be obtained as:

$$D_p = |\Delta W_A/n_A+\Delta W_B/n_B+E_p+Z_A'Z_B'/R_{AB} -1/2K_p^{-1}\,Q_p^{\circ 2}+\lambda_p| \tag{12}$$

Since the variation in the promotion energy, ΔW, from molecule to molecule is generally small, at least for similar molecules, as has been discussed in Ref. 2, each term of Eq. 12 except the last term may be regarded as specific for the bond p. The λ_p is a small correction term which is mainly due to the interaction energy between the bond p and its adjacent bonds or lone pairs. However, this term is implicitly included in the empirical bond energy. Actually, for the branched isomers of hydrocarbons, small deviations in the empirical bond energies have been reported.[15] For a series of similar molecules such as hydrocarbons, however, this relative variation may be expected to be quite small, because the λ_p values are nearly constant. The D_p may thus be regarded as the empirical bond energy. To an even cruder approximation, the D_p may be rewritten as

$$\begin{aligned}D_p \sim |\,&\Delta W_A/n_A+\Delta W_B/n_B+1/4(J_{A,pA,p}\\ &+J_{B,pB,p})+(B:A,\ pA,\ p)+(A:B,pB,p)\\ &+1/2J_{A,pB,p}+2\gamma_p(1+S_p)^{-1}\\ &-1/2K_pQ_p^{\circ 2}+\lambda_p\,|\end{aligned} \tag{13}$$

In this approximation, it is shown that the lone pairs on both the atoms A and B make no contributions to the bond energy except indirectly. The bond energy is then regarded as specific for the bond only.

Another necessary condition for bond additivity is that the length of one particular bond be the same in different positions or molecules. This condition is satisfied for saturated compounds, but it is well known that the bond lengths in nonsaturated compounds may vary considerably. It may thus be concluded that bond energies are not only additive but also remain constant for different molecules in saturated compounds.

II. The Bond Additivity of the Dipole Moment.—If nuclei and inner-shell electrons are regarded as point charges, the molecular dipole moment, μ, may be given by:

$$\mu = e[\langle \boldsymbol{r}_e\rangle - \sum_a Z_a'\boldsymbol{R}_a] \tag{14}$$

where

$$\langle \boldsymbol{r}_e\rangle = \langle \Phi^* |\, \boldsymbol{r}_e \,| \Phi\rangle$$

The $\boldsymbol{R}_a$ and $\boldsymbol{r}_e$ are the radius vectors which represent the position of the nucleus of the atom a and the electrons respectively, and Φ is the molecular wave function given by Eq. 1 of Ref. 1. By using the previous results,[1] we obtain

$$\langle \boldsymbol{r}_e\rangle = 2\sum_i[\boldsymbol{r}_i^{+} - 2\sum_k \boldsymbol{r}_{ik}^{+-}\ \beta_{ik}^{+-}/(\varepsilon_k^{-}-\varepsilon_i^{+})$$

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[12] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, N. Y. (1945).

[13] See also Ref. 11.

[14] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

[15] J. R. Platt, *J. Chem. Phys.*, **15**, 419 (1947).

$$+\sum_{\mathrm{kl}}\boldsymbol{r}_{\mathrm{kl}}^{-}\,\beta_{\mathrm{ik}}^{+-}\,\beta_{\mathrm{il}}^{+-}/(\varepsilon_{\mathrm{k}}^{-}-\varepsilon_{\mathrm{i}}^{+})\;(\varepsilon_{\mathrm{l}}^{-}-\varepsilon_{\mathrm{i}}^{+})] \tag{15}$$

where

$$\boldsymbol{r}_{\mathrm{ik}}^{+-}=\langle\psi_{\mathrm{i}}^{+}\,|\boldsymbol{r}_{\mathrm{e}}|\,\psi_{\mathrm{k}}^{-}\rangle,\qquad \boldsymbol{r}_{\mathrm{i}}^{+}\equiv\boldsymbol{r}_{\mathrm{ii}}^{++},\ \text{etc.}$$

The subscript *i* refers to the unperturbed filled MO, and the subscripts *k* and 1, to the unperturbed empty MO respectively. The last term is relatively small; it will, therefore, be neglected. According to a discussion similar to that of the previous section, we obtain[10]

$$\sum_{\mathrm{i}}\boldsymbol{r}_{\mathrm{i}}^{+}=\sum_{\mathrm{p}}\overline{\boldsymbol{r}}_{\mathrm{p}}=\sum_{\mathrm{p}}\boldsymbol{r}_{\mathrm{p}}-\sum_{\substack{\mathrm{pq}\\(\mathrm{p}\neq\mathrm{q})}}S_{\mathrm{pq}}\boldsymbol{r}_{\mathrm{pq}} \tag{16}$$

where the $\overline{\boldsymbol{r}_{\mathrm{p}}}$ and $\boldsymbol{r}_{\mathrm{p}}$ are the corresponding quantities for OBO p and BO p respectively. Equation 15 may now be reduced to:

$$\langle\boldsymbol{r}_{\mathrm{e}}\rangle=2\sum_{\mathrm{p}}\boldsymbol{r}_{\mathrm{p}}-2\sum_{\substack{\mathrm{pq}\\(\mathrm{p}\neq\mathrm{q})}}S_{\mathrm{pq}}\boldsymbol{r}_{\mathrm{pq}}$$

$$-4\sum_{\mathrm{ik}}\boldsymbol{p}_{\mathrm{ik}}^{+-}\,\beta_{\mathrm{ik}}^{+-}/(\varepsilon_{\mathrm{k}}^{-}-\varepsilon_{\mathrm{i}}^{+}) \tag{17}$$

The first term may be assigned to a specific bond or a lone pair, but this is not necessarily true for the other terms. By using Eqs. 18 and 21 of Ref. 1, $\boldsymbol{r}_{\mathrm{p}}$ may be represented as:

$$\begin{aligned}\boldsymbol{r}_{\mathrm{p}}=1/2\,[(1-\overline{Q}_{\mathrm{p}}-F_{\mathrm{p}}S_{\mathrm{p}})\boldsymbol{r}_{\mathrm{A,p}}+(1+\overline{Q}_{\mathrm{p}}\\ -F_{\mathrm{p}}S_{\mathrm{p}})\boldsymbol{r}_{\mathrm{B,p}}+2F_{\mathrm{p}}\boldsymbol{r}_{\mathrm{A,pB,p}}=1/2\,[(\boldsymbol{R}_{\mathrm{A}}+\boldsymbol{R}_{\mathrm{B}})\\ +(\boldsymbol{r}_{\mathrm{A,p}}^{\mathrm{x}}+\boldsymbol{r}_{\mathrm{B,p}}^{\mathrm{x}})+\overline{Q}_{\mathrm{p}}(\boldsymbol{R}_{\mathrm{p}}+\boldsymbol{r}_{\mathrm{B,p}}^{\mathrm{x}}-\boldsymbol{r}_{\mathrm{A,p}}^{\mathrm{x}})\\ -F_{\mathrm{p}}\boldsymbol{V}_{\mathrm{p}}]\end{aligned} \tag{18}$$

where

$$\boldsymbol{V}_{\mathrm{p}}=S_{\mathrm{p}}(\boldsymbol{r}_{\mathrm{A,p}}+\boldsymbol{r}_{\mathrm{B,p}})-2\boldsymbol{r}_{\mathrm{A,pB,p}}$$

$$\boldsymbol{r}_{\mathrm{U,p}}=\boldsymbol{R}_{\mathrm{U}}+\boldsymbol{r}_{\mathrm{U,p}}^{\mathrm{x}}\qquad(\mathrm{U}=\mathrm{A,B})$$

The $\boldsymbol{R}_{\mathrm{U}}$ and $\boldsymbol{r}_{\mathrm{U,p}}^{\mathrm{x}}$ stand for the radius vector for the nucleus of the atom U and the atomic dipole vector of AO U, p respectively. $\boldsymbol{R}_{\mathrm{p}}$ is the vector pointing from nucleus A to nucleus B along the bond p with the distance $\boldsymbol{R}_{\mathrm{AB}}$ as its magnitude. In a similar way, we have for lone pairs:

$$\boldsymbol{r}_{\mathrm{f(a)}}=\boldsymbol{R}_{\mathrm{a}}+\boldsymbol{r}_{\mathrm{f(a)}}^{\mathrm{x}} \tag{19}$$

We thus obtain:

$$\begin{aligned}2\sum_{\mathrm{p}}\boldsymbol{r}_{\mathrm{p}}\equiv2\,({\textstyle\sum_{\mathrm{p}}'}\boldsymbol{r}_{\mathrm{p}}+{\textstyle\sum_{\mathrm{f}}'}\boldsymbol{r}_{\mathrm{f}})=\sum_{\mathrm{a}}Z_{\mathrm{a}}'\boldsymbol{R}_{\mathrm{a}}+\sum_{\mathrm{a}}\boldsymbol{r}_{\mathrm{a}}^{\mathrm{x}}\\ +{\textstyle\sum_{\mathrm{p}}'}\overline{Q}_{\mathrm{p}}(\overline{\boldsymbol{R}}_{\mathrm{p}}+\boldsymbol{r}_{\mathrm{B,p}}^{\mathrm{x}}-\boldsymbol{r}_{\mathrm{A,p}}^{\mathrm{x}})-{\textstyle\sum_{\mathrm{p}}'}F_{\mathrm{p}}\boldsymbol{V}_{\mathrm{p}}\end{aligned} \tag{20}$$

where

$$\boldsymbol{r}_{\mathrm{a}}^{\mathrm{x}}=\sum_{\mathrm{U,p(a)}}{}'\,\boldsymbol{r}_{\mathrm{U,p(a)}}^{\mathrm{x}}+2\sum_{\mathrm{f(a)}}{}'\,\boldsymbol{r}_{\mathrm{f(a)}}^{\mathrm{x}} \tag{21}$$

$\sum_{\mathrm{p}}'$ and $\sum_{\mathrm{f}}'$ denote summations over bonds and lone pairs exclusively, and U, p(a) stands for the AO belonging to the atom a and the bond p. Since the valence AO of the atom a may be an equivalent set in the present treatment, the total atomic dipole of the atom a given by Eq. 21 may be rewritten as

$$\boldsymbol{r}_{\mathrm{a}}^{\mathrm{x}}=\sum_{\mathrm{f(a)}}{}'\,\boldsymbol{r}_{\mathrm{f(a)}}^{\mathrm{x}} \tag{22}$$

This shows that the total atomic dipole vanishes except for the lone pair dipole. By using Eqs. 17, 20 and 22, the molecular dipole moment, μ, may now be written as

$$\begin{aligned}\mu=e\,[{\textstyle\sum_{\mathrm{f}}'}\boldsymbol{r}_{\mathrm{f}}+{\textstyle\sum_{\mathrm{p}}'}\overline{Q}_{\mathrm{p}}(\boldsymbol{R}_{\mathrm{p}}+\boldsymbol{r}_{\mathrm{B,p}}^{\mathrm{x}}-\boldsymbol{r}_{\mathrm{A,p}}^{\mathrm{x}})-{\textstyle\sum_{\mathrm{p}}'}F_{\mathrm{p}}\boldsymbol{r}_{\mathrm{p}}\\ -2\sum_{\substack{\mathrm{pq}\\(\mathrm{p}\neq\mathrm{q})}}S_{\mathrm{pq}}\boldsymbol{r}_{\mathrm{pq}}-4\sum_{\mathrm{ik}}\boldsymbol{r}_{\mathrm{ik}}^{+-}\beta_{\mathrm{ik}}^{+-}/(\varepsilon_{\mathrm{k}}^{-}-\varepsilon_{\mathrm{i}}^{+})]\end{aligned} \tag{23}$$

If we restrict ourselves to the case of small bond polarity, apart from the last two terms of Eq. 23, which may not be specific for localized bonds or lone pairs, the bond moment, μ_{p}, may be defined by:

$$\begin{aligned}\mu_{\mathrm{p}}=e\,[\{(\sum_{\mathrm{f(A)}}{}'\,\boldsymbol{r}_{\mathrm{f(A)}}^{\mathrm{x}})_{\mathrm{p}}+(\sum_{\mathrm{f(B)}}{}'\,\boldsymbol{r}_{\mathrm{f(B)}}^{\mathrm{x}})_{\mathrm{p}}\}-\boldsymbol{V}_{\mathrm{p}}/(1+S_{\mathrm{p}})\\ +\overline{Q}_{\mathrm{p}}(\boldsymbol{R}_{\mathrm{p}}+\boldsymbol{r}_{\mathrm{B,p}}^{\mathrm{x}}-\boldsymbol{r}_{\mathrm{A,p}}^{\mathrm{x}})+1/2\overline{Q}_{\mathrm{p}}\boldsymbol{V}_{\mathrm{p}}\}]\end{aligned} \tag{24}$$

where $e(\sum_{\mathrm{f(A)}}{}'\,\boldsymbol{r}_{\mathrm{f(A)}}^{\mathrm{x}})_{\mathrm{p}}$ and $e(\sum_{\mathrm{f(B)}}{}'\,\boldsymbol{r}_{\mathrm{f(B)}}^{\mathrm{x}})_{\mathrm{p}}$ are the components of the lone pair moments of the atoms A and B respectively in the direction of the bond p. The first term, therefore, is the part of the atomic dipole due to the lone pairs; it vanishes for atoms such as tetrahedral carbon. It follows that in the atomic dipoles only the lone pairs contribute to the bond moments if we neglect the indirect contributions from the other terms of Eq. 24. This conclusion agrees with previous works,[9,16,17] and the significance of the lone pair dipole has been emphasized by several authors.[9,16–19] The second term is the homopolar dipole moment which is especially significant for homopolar bonds, and the third term is the heteropolar dipole, which is due to the bond polarity. In Mulliken's approximation[20] the homopolar dipole term vanishes; in addition, if the atomic dipole is neglected, we obtain

$$\mu_{\mathrm{p}}=e\overline{Q}_{\mathrm{p}}\boldsymbol{R}_{\mathrm{p}} \tag{25}$$

The bond moment, μ_{p}, then coincides with the

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16) J. A. Pople, *Proc. Roy.* Soc., **A202**, 323 (1950).

17) H. F. Hameka and A. M. Liquori, *Mol. Phys.*, **1**, 9 (1958).

18) D. Z. Robinson, *J. Chem. Phys.*, **17**, 1022 (1949).

19) H. Hamano and H. F. Hameka, *Tetrahedron*, **18**, 985 (1962).

20) R. S. Mulliken, *J. Chem. Phys.*, **46**, 497, 675 (1949).

corresponding empirical quantity.[6] This approximation, however, is generally not correct. The significance of the homopolar dipole has also been stressed by several authors.[8,18,19,21-23] For instance, the actual calculation[8,17,23] of the bond moment of the CH bond, which is regarded as nearly homopolar, yields a large value for this term, even if the atomic dipole is neglected. In spite of these facts, the concept of bond moments as given by Eq. 25 has proved to be a useful tool in the interpretation of experimental dipole moments.

The quantum mechanical theory does not seem to be in agreement with this. However, the discrepancy may be interpreted as follows: A vector summation over the whole molecule of the atomic dipoles and homopolar dipoles of Eq. 24 may tend to cancel some of the terms that cause the discrepancies. This statement may not have a general validity, but it seems to be correct for many organic compounds where all the bonds connected to one central atom usually point in opposite directions. The same inference may be true for the last two terms of Eq. 23; they also tend to cancel each other. In fact, the empirical bond moments are usually much smaller than those given by Eq. 24; sometimes their directions are even opposite to the theoretical ones.[23] In addition, if it is borne in mind that the empirical bond moments are not uniquely defined and that it is permissible to omit the quantities which are cancelled in summing over the whole molecule as long as this sum reproduces the total molecular dipole moment, it is not surprising that the theoretical and empirical bond moments are not in agreement with one another.

We will now consider the influence of the inductive effect on the bond moment. Since the Q_p consists of the specific Q_p° and induced Q_p' polarities,[1] if follows from Eq. 24 that the induced bond moment is nearly proportional to the induced polarity, Q_p'. The intra-bond electron transfers caused by the inductive effect occur as in Figs. 1 or 2 of Ref. 1, so the vector sum of the induced bond moment throughout the molecule may be additive. Besides, each bond moment is sensitive to variations in the hybridization. The bond moment, μ_p, may thus be defined as different in different molecules, and the molecular dipole moments may depend greatly on the inductive effect. The dipole moments of the series of CH_3X, CH_2X_2 and CHX_3 (X=halogens), which are tabulated in Table II of Ref. 2, seem to support this argument; if the CX and CH bond moments in these series were constant, the CH_2X_2 molecules would have the larger dipole moments and the CH_3X and CHX_3 molecules would have the same smaller moments. The experimental data, however, show that the dipole moments of these series decrease in the above order. This discrepancy has already been discussed in the preceding paper.[2] Another example has also been shown in Ref. 2. The assumption of a uniform bond moment, therefore, may be a poor approximation when the inductive effect is taken into consideration. Bond moments do not remain constant for different molecules, whereas for bond energies they do.

The previous argument assumes again that all bond lengths are constant; the validity of this assumption has already been discussed in the previous section.

Discussion

In the present treatment, it has been shown that the bond additivity is valid only if the delocalization of the bond electrons in σ electron systems is small. At first sight, therefore, it appears that the bond additivity is based only on the localization of the electrons in their bonds. The justification of the bond additivity, however, is essentially due to the following: If the BO are taken as a basis, such physical quantities as heats of formation and dipole moments may be represented by the matrices of the corresponding operators with respect to the BO. By means of a unitary transformation these matrices may be diagonalized; the heat of formation or the dipole moment of the molecule is then obtained as the trace of the matrix. After the transformation, each diagonal element may formally be assigned to one specific bond. However, since the trace of the matrix remains invariant,[24] we may also take the diagonal elements of the original matrix as each describing a separate bond. Their sum will then correctly represent either the total heat of formation or the dipole moment of the molecucle, even though the diagonal elements bofore and after the unitary transformation are not necessarily the same.[25] For bond

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[21] R. S. Mulliken, *J. Chem. Phys.*, 3, 573 (1935).

[22] C. A. Coulson and M. T. Rogers, ibid., 35, 593 (1961).

[23] H. Hamano, ibid., 34, 1678 (1961).

[24] Actually this is true only for the localized MO, but since the orbitals are sufficiently localized in each specific bond or lone pair, it is a reasonably good approximation for the BO also.

[25] This is equivalent with the principle of spectroscopic stability as introduced by Born et al. (M. Born, W. Heisenberg and P. Jordan, *Zeits. f. Physik*, 35, 557 (1926)). In fact, the theoretical background for many semi-empirical models in physical and chemical problems, especially for sum rules, is due to this principle; the details and some examples appear in Van Vleck's book (J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Univ. Press, London (1932)), in connection with the principle of spectroscopic stability.

energies this was discussed in Ref. 1 ; for bond moments it is shown in Eq. 16.

The validity of the concept of bond additivity is due not only to the facts above, but also to the accidental cancellations when summing over the whole molecule. These cancellations occur in different ways for different quantities and then determine whether the bond quantities are constant or not from molecule to molecule, the former case for bond energies and the latter for bond moments. These facts often make the empirical bond quantities appear to be different quantities from those obtained quatum-mechanically.[26] This is especially true for bond moments. In practice, if the bond quatities are constant for different molecules, we say that the bond additivity rule holds. In this sense, dipole moments do not follow the additivity rule.

Chemists have often discussed the physical quantities of molecules by using the "*chemical bond*" concept. At first sight it seems to follow from our considerations that this concept is not meaningful theoretically because the bond orbitals are not eigenfunctions and molecular-observable quantities should be derived as expectation values of the molecular wave function. The present argument, however, shows that the chemical bond is a reasonable concept as long as it is used to discuss properties belonging to the total molecule. The situation is the same for the valence AO's of atoms ; they are also equivalent orbitals which are not eigenfunction. The concept of these localized orbitals is thus very useful for chemists, even though it does not have physical significance. It is also worth noting that the concept of bond is not directly connected with the empirical bond additivity rules, as has been discussed above.

Summary

The aditivity rules for bond energies and bond moments are discussed on the basis of a previously-proposed theory. The results show that the apparent additivities are partially caused by accidental cancellations when summing over the molecule and essentially by the invariance of the trace of the matrix representing the molecular quantity. Bond energies are then constant in different molecules, whereas bond moments are not, mainly because of the inductive effect.

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[26] The contribution of lone pairs then vanishes in the approximation of Eq. 13 for heats of formation and does not vanish for dipole moments, its influence is implicitly accounted for by adjusting the empirical value for the bond quantity.