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A New Version of Inclusion of Overlap Charges in ω-Technique. π-Bond Energies, Heats of Formation, and Resonance Energies of Conjugated Hydrocarbons

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With systematic approximations to Roothaan equation it has been possible to deduce the IOC-ω-technique (inclusion of overlap charges in ω-technique) which apparently approximates the SCF-equations by bringing in an approximate correction for the two center-two electron repulsion integrals and represents a better version of PPP (Pariser-Parr-Pople) method by involving the hybrid integrals which have been completely neglected in PPP-approximations. In the present communication a new version of IOC-ω-Technique has been used for evaluating the π-bond energies, heats of formation and resonance energies of some conjugated hydrocarbons. The calculated values are found to be in excellent agreement with the experimental data and with some previously calculated values.

In the framework of LCAO-MO approximations Roothaan[1] has given $F_{\mu\nu}$ as,

$$F_{\mu\nu} = H^C_{\mu\nu} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}\{(\mu\nu, \lambda\sigma) - 1/2(\mu\lambda, \nu\sigma)\}, \tag{1}$$

where $H^C_{\mu\nu}$ is the matrix element involving core Hamiltonian such that,

$$H^C_{\mu\nu} = \int\phi_\mu\left(-\frac{h^2}{8\pi^2m}\right)\nabla^2 - \sum_\sigma V_\sigma\Big)\phi_\nu \mathrm{d}\tau, \tag{2}$$

and $(\mu\nu, \lambda\sigma)$ the electron repulsion integral represented as,

$$(\mu\nu, \lambda\sigma) = \iint\phi_\mu(1)\,\phi_\nu(1)\,\frac{e^2}{r_{12}}\,\phi_\lambda(2)\,\phi_\sigma(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2. \tag{3}$$

It has been shown[2] that if all electron repulsion integrals are neglected except for one centre integrals $(\mu\mu, \mu\mu)$, two centre integrals $(\mu\mu, \sigma\sigma)$ and the hybrid integrals $(\mu\mu, \mu\sigma)$, since the other integrals are of very small magnitude, then the diagonal matrix elements of Eq. 1 reduces to,

$$\begin{aligned} F_{\mu\mu} &= H^C_{\mu\mu} + 1/2\,p_{\mu\mu}(\mu\mu, \mu\mu) + 1/2\sum_{\sigma\neq\mu} p_{\mu\sigma}(\mu\mu, \mu\sigma) \\ &\quad + \sum_{\mu\neq\sigma} q_\sigma\,(\mu\mu, \sigma\sigma) \\ &= H^C_{\mu\mu} + 1/2\sum p_{\mu\sigma}(\mu\mu, \mu\sigma) + \sum_{\mu\neq\sigma} q_\sigma(\mu\mu, \sigma\sigma). \end{aligned} \tag{4}$$

However, the coulomb integral, $H^C_{\mu\mu}$, neglecting the penetration integral, is approximated as,[3]

$$H^C_{\mu\mu} = I_\mu - \sum_{\mu\neq\sigma}(\mu\mu, \sigma\sigma)$$

where I_μ is the valence state ionization potential of an electron associated with atom μ. Equation 4 therefore leads to,

$$F_{\mu\mu} = I_\mu + 1/2\sum_\sigma p_{\mu\sigma}(\mu\mu, \mu\sigma) + \sum_{\sigma\neq\mu}(q_\sigma - 1)(\mu\mu, \sigma\sigma). \tag{5}$$

Since the integral $(\mu\mu, \mu\sigma)$ obviously depends upon the charge distribution $\phi_\mu\,\phi_\sigma$ so that it can be made proportional to the overlap integral $S_{\mu\sigma}$,

$$(\mu\mu, \mu\sigma) = 2w_\mu\,s_{\mu\sigma} \tag{6}$$

where ω_μ is a proportionality constant which may be written as,

$$\omega_\mu = 1/2(\mu\mu, \mu\mu), \tag{7}$$

in case of $\mu = \sigma$.

However, ω_μ is treated as an empirical parameter in order to cover up the deficiencies in the method due to several approximations involved. Inserting Eq. 6 in Eq. 5,

$$F_{\mu\mu} = I_\mu + \omega_\mu\sum p_{\mu\sigma}\,s_{\mu\sigma} + \sum_{\sigma\neq\mu}(q_\sigma - 1)\,(\mu\mu, \sigma\sigma). \tag{8}$$

At this stage a new parameter α_μ has been defined as,

$$\alpha_\mu = I_\mu + \omega_\mu.$$

In terms of this parameter Eq. 8 will assume the following form,

$$\begin{aligned} F_{\mu\mu} &= \alpha_\mu + \omega_\mu\,(\sum_\sigma p_{\mu\sigma}\,s_{\mu\sigma} - 1) \\ &\quad + \sum_{\sigma\neq\mu}(q_\sigma - 1)\,(\mu\mu, \sigma\sigma). \end{aligned} \tag{9}$$

For most of the molecules last term of Eq. 9 would be very small and in fact will be equal to zero for alternant hydrocarbons. Therefore, this last term may be neglected and consequently Eq. 9 will assume the following form,

$$\begin{aligned} F_{\mu\mu} &= \alpha_\mu + \omega_\mu\,(\sum_\sigma p_{\mu\sigma}\,s_{\mu\sigma} - 1) \\ &= \alpha_\mu + \omega_\mu\,\{1/2\sum_\sigma(p_{\mu\sigma}\,s_{\mu\sigma} + p_{\sigma\mu}\,s_{\sigma\mu}) - 1\}. \end{aligned} \tag{10}$$

The last line of Eq. 10 follows from the fact that in the expansion of Eq. 1 both $(\mu\mu, \mu\sigma)$ and $(\mu\mu, \sigma\mu)$ type integrals will occur but since there is no difference between them the factor 1/2 has been included to avoid the counting of them twice. If ω_μ is treated as a negative parameter Eq. 10 will become,

$$F_{\mu\mu} = \alpha_\mu + \omega_\mu\,\{1 - 1/2\sum_\sigma(p_{\mu\sigma}\,s_{\mu\sigma} + p_{\sigma\mu}\,s_{\sigma\mu})\}, \tag{11}$$

which has been used in our calculation as diagonal matrix element. $F_{\mu\mu}$ as derived in Eq. 1 approximates the SCF equations by bringing in an approximate correction for the two centre-two electron repulsion integral and represents a better version of PPP-method since it involves hybrid integrals which have been completely neglected in PPP-metod and which are in no way negligible as they can be as large as 3.5 eV.[4] The success of the technique can also be attributed to the fact that the inclusion of overlap charges permits the ω-technique to make use of orthogonal atomic orbitals (OAO's) rather than usual nonorthogonal slater type atomic orbitals (STAO's). The ω-technique, which has been put to successful use by Aihara,[5] can be said to be a simplified version of PPP-method (for example see Doggett[6]) which is based on zero differential overlap (ZDO) approximations of Pariser, Parr and Pople[3,7] and since these approximations are valid only over OAO's and not over usual non-orthogonal STAO's, the use of OAO's is essentially warranted in it. It has been shown by Gupta[8] that this necessity in ω-technique is fulfilled by inclusion of overlap charges. This is arrived at by deducing the IOC-ω-technique (inclusion of overlap charges in ω-technique) in the framework of Lowdin's OAO's. In the present communication the following form of the off diagonal matrix element has been used for the first time in the framework of IOC-ω-technique,

$$F_{\mu\nu} = K S_{\mu\nu} (F_{\mu\mu} \cdot F_{\nu\nu})^{1/2}, \tag{12}$$

where K is a dimensionless constant and $S_{\mu\nu}$ are the overlap integrals. Since $F_{\mu\nu}$ represents the energy of interaction between atomic orbitals μ and ν, the simple arithmatic mean, an approximation used by Wolfsberg and Helmholtz,[9] evidently takes into account only an average interaction between atomic orbitals whereas a use of geometric mean[10] will incorporate all the possible interactions between different atomic orbitals.

In most of the semiempirical π-electron calculations, using variant of the Pariser-Parr-Pople[3,7] (PPP-method), the choice of parameters required to give optimum agreement with experiment is specific for a particular property, or is valid for a specific class of compounds, and cannot therefore, generally be extended to other molecular properties or to different class of molecules. In the present work a set of parameters has been developed which when applied to a given molecular property, *e.g.* ionization potential produces good results and also give satisfactory results when used to calculate other properties, *e.g.* electron affinity, π-bond energies, heats of formation and resonance energies of different class of compounds.

π-Bond Energy. In molecular orbital theory the π-electronic energy of a molecule is given by,

$$E_\pi = \text{Total molecular orbital energy}$$
$$= \sum_\mu \sum_\nu p_{\mu\nu} F_{\mu\nu}. \tag{13}$$

Substituting the values of $F_{\mu\mu}$ and $F_{\mu\nu}$ from Eqs. 11 and 12 into Eq. 13, we shall get the following expression for the total π-elecronic energy,

$$E_\pi = \sum_\mu q_\mu \alpha + \omega \sum_\mu q_\mu (1-q_\mu) - \omega s \sum_\mu \sum_{\sigma \neq \mu}$$
$$q_\mu p_{\mu\sigma} + KS \sum_\mu \sum_\nu p_{\mu\nu} \{(\alpha + \omega(1-q_\mu)$$
$$- \omega S \sum_\sigma p_{\mu\sigma}) (\alpha + \omega(1-q_\nu) - \omega S \sum p_{\nu\sigma})\}^{1/2}. \tag{14}$$

Now, consider the energy liberated when n carbon atoms with p-electrons combine to form π-bonds, *i.e.* energy ($E_{\pi b}$). The total π-electronic energy of a molecule is given by the algebraic sum of the energy of electrons in p-orbital of widely separated carbon atoms and the π-bond energy ($E_{\pi b}$). The former may be equated to $\sum q_\mu \alpha$. Hence, the remaining terms of Eq. 14 give π-bond energy. For alternant hydrocarbons with $q_\mu = 1$, we have,

$$E_{\pi b} = -\omega S \sum_\mu \sum_{\sigma \neq \mu} q_\mu p_{\mu\sigma} + 2KS \sum\sum_{\mu < \nu} p_{\mu\nu}$$
$$\{(\alpha - \omega S \sum p_{\mu\sigma})(\alpha - \omega S \sum p_{\nu\sigma})\}^{1/2}. \tag{15}$$

Heat of Formation. The heat of formation of a molecule in its equilibrium configuration is the additive sum of the bond energies. The total bond energy of a molecule is given by the sum of the total σ-bond energy, $E_{\sigma b}$ and total π-bond energy, $E_{\pi b}$. The following expression provides a simple route to calculate heats of formation of hydrocarbons.

$$\Delta H_f = E_{\sigma b} + E_{\pi b}$$
$$= N_C E_{CC} + N_H E_{CH} + E_{\pi b}, \tag{16}$$

where E_{CC} and E_{CH} are the bond energies of C–C and C–H bonds respectively and N_C and N_H are the number of C–C and C–H bonds respectively.

Resonance Energy. If a compound possesses more than one structure, the resonance energy is regarded as a physical measure of the most stable structure relative to other possible structure. Among the various possible definitions of the term resonance energy, the most important is one due to Mulliken and Parr[11] (empirical resonance energy), which is taken as the differences between the bond energies of structure I and II,

$$E_R = E_{b(I)} - E_{b(II)}, \tag{17}$$

where I represents an aromatic structure with all bonds equal to 1.40 Å and II represents a structure with alternating C–C bond length and C=C bond length. The bond energies may be calculated with the help of the following equations,

$$E_{b(I)} = NE_C + N_H E_H + E_{\pi b(I)}, \tag{18}$$

and

$$E_{b(II)} = N_1 E_1 + N_2 E_2 + N_H F_H. \tag{19}$$

In which $E_{\pi b(I)}$ is the π-bonding energy of structure I and $N = N_1 + N_2$. E_1 and E_2 are the energies of a C–C bond of length 1.48 Å and C=C bond of length 1.34 Å respectively. N_1, N_2, N_H, and E_H represent the number of single and double bonds and number of C–H bonds and energy of carbon–hydrogen bonds respectively.

Now, since the values of E_1 and E_2 are very uncertain, we shall use the following scheme instead of using them directly,

$$E_R = NA_0 + (N_1 - N_2) A_1 + E_{\pi b(I)} \tag{20}$$

where,

$$A_0 = E_C - \frac{E_1 + E_2}{2}, \tag{21}$$

$$A_1 = \frac{E_2 - E_1}{2}. \tag{22}$$

However, A_0 and A_1 are to be treated as empirical parameters.

Values of Parameters. In the present communication, it has been assumed that the overlap integral $S_{\mu\nu}$ vanishes for non-neighbouring μ, ν and it

Table 1. π-Bond energies and heats of formation of alternant hydrocarbons

Compound	$E_{\pi b}$/eV	Present work	Ref. 16	Ref. 17	Experimetal Ref. 18
Benzene	7.91	57.29	57.52	57.16	57.16
Naphthalene	13.43	90.67	90.516	90.61	90.61
Anthracene	18.95	124.05	123.655	123.89	123.93
Naphthacene	24.44	157.40	156.096	157.11	157.56
Biphenyl	16.10	109.80	—	109.75	109.76
Styrene	10.28	76.12	—	75.91	75.83
Stilbene	18.57	128.73	—	128.54	128.48
Pyrene	22.03	138.73	138.956	138.62	138.88
Perylene	27.64	172.00	169.599	172.15	172.04
Phenanthrene	19.07	124.17	123.460	124.22	124.20
Triphenylene	25.03	157.99	156.624	157.94	157.76
Benzo [*c*] phenanthrene	24.68	157.64	156.067	157.77	157.56
Benz [*a*] anthracene	24.60	157.56	—	157.58	157.49
Chrysene	24.68	157.64	156.157	157.77	157.73
Av. dev.		0.12	0.765	0.11	

Table 2. Empirical resonance energies of alternant hydrocarbons

Compound	Present work	Ref. 19			Ref. 20	Experimental Ref. 21
		Huckel	Pople	SPO		
Benzene	1.55	1.318	1.318	1.318	1.560	1.553
Naphthalene	2.61	2.312	2.429	2.258	1.645	2.631
Anthracene	3.67	3.365	3.382	3.039	4.147	3.601
Naphthacene	4.70	4.206	4.278	3.750	5.126	4.744
Biphenyl	3.16	—	—	—	—	—
Styrene	1.80	1.80	—	—	—	—
Stilbene	3.51	—	—	—	—	—
Pyrene	4.41	—	—	—	—	4.696[a]
Perylene	5.56	4.998	5.713	4.961	4.779	5.447[a]
Phenanthrene	3.79	3.372	3.750	3.386	4.020	3.937
Triphenylene	5.29	4.479	5.236	4.643	4.416	5.076
Benzo [*c*] phenanthrene	4.94	—	—	—	4.822	4.727
Benz [*a*] anthracene	4.86	—	—	—	—	4.813
Chrysene	4.94	—	—	—	4.918	5.024
Av. dev.	0.09		0.246		0.286	

a) Ref. 22.

has a constant value S for μ, and ν directly bonded. S has been assigned a value of 0.25. ω has been taken to 1.4. Both the values have been extensively used by several workers.[12,13] K has been assigned a value of 1.634, which is very close to its value quoted in literature.[14] E_{CC} and E_{CH} are taken as 3.80 and 4.43 respectively, as proposed by Dewar and Gleicher.[15] A_0 and A_1 have been assigned values as -1.06 and 0.84 respectively. α has been taken to be 7.00.

Results and Discussion

In Table 1, we have listed the values of heat of formation obtained with Eqs. 15 and 16 along with some previously calculated values[16,17] and with available experimental values.[18] A close study of Table 1, shows that our calculated values are generally in excellent agreement with the experimental values. The values calculated by the present method (av.dev. $=0.12$) are also in good agreement with Dellano[17] (av.dev. $=$ 0.11) and are better than those calculated by Srivastava[16] (av.dev. $=0.765$). Table 2, enlists the empirical resonance energy calculated by the present method along with some previously calculated values[19,20] and the relevant experimental data.[21,22] From Table 2, it is amply clear that the values obtained by the present method are in excellent agreement with the observed experimental values. The values calculated by the present technique (av. dev. $=0.09$) are better than those calculated by Srivastava[20] (av. dev. $=$ 0.286) and Dewar[19] (av. dev. $=0.246$) PPP-method.

It is worth mentioning that the same set of parameters have been used for the calculation of different ground state properties of various class of compounds. Thus the values obtained are in good agreement with experimental values.

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