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NOTES ON KUHN'S ω'' MOLECULAR ORBITAL METHOD

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Abstract—(1) It is shown that, contrary to statements sometimes made, it is perfectly possible to obtain consistent sets of charges in Kuhn's ω'' molecular-orbital method, whatever the values of the parameters ω, ω', ω''.

(2) Particular applications are made to the benzyl cation, and to the non-alternants fulvene, heptafulvene and azulene. It appears that including the ω-terms decreases the magnitude of the largest of the net atomic charges as calculated by the simple Hückel method, and results in an overall smoothing-out process. Further inclusion of the ω'-terms continues this smoothing-out process, but inclusion of the ω''-terms may sometimes slightly reverse this process.

(3) The charge distributions obtained for fulvene and azulene in (1) and (2) lead to molecular dipole moments which are still much too large.

In view of (3) it is not clear that the additional work involved in the inclusion of ω' and ω'' is justified by the greater accuracy thus obtained.

INTRODUCTION

THE ω-method was introduced by Wheland and Mann,[1] Moffitt,[2] Streitwieser,[3] Pritchard and Sumner[4] and others to make some allowance for the net charge on an atom in a conjugated or aromatic system, when writing down the appropriate Coulomb term α. If q_r is the total number of π-electrons on atom r, we write

$$\alpha_r \equiv \alpha_r(q_r) = \alpha_0 + \omega\beta_0(1 - q_r) \tag{1}$$

In this expression α_0 is the Coulomb term when $q_r = 1$, β_0 is a standard resonance integral, and ω has the value $\omega = 1{\cdot}4$, chosen to provide a best fit with observed and calculated ionization potentials. Recently[5] Kuhn has drawn attention to the influence of first-neighbour atoms s, and of second neighbours t, writing instead of (1) the more general equation

$$\alpha_r \equiv \alpha_r(q_r, q_s, q_t) = \alpha_0 + \omega\beta_0(1 - q_r) + \sum_s \omega'\beta_0(1 - q_s) + \sum_t \omega''\beta_0(1 - q_t) \tag{2}$$

If we put

$$c_r = 1 - q_r \tag{3}$$

for the net charge on atom r, (2) may be written

$$\alpha_r \equiv \alpha_r(c_r, c_s, c_t) = \alpha_0 + \omega\beta_0 c_r + \sum_s \omega'\beta_0 c_s + \sum_t \omega''\beta_0 c_t \tag{4}$$

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[1] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).
[2] W. C. Moffitt, *Proc. Roy. Soc.* **A196**, 511 (1949).
[3] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **82**, 4123 (1960); *J. Phys. Chem.* **66**, 368 (1962); *Molecular Orbital Theory for Organic Chemists*, Wiley, New York (1961).
[4] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.* **A235**, 136 (1956).
[5] H. Kuhn, *Tetrahedron* **19**, Supplement 2, 437 (1963).

The parameters ω, ω' and ω'' measure approximately the electrostatic potential at nucleus r of charge on atoms r, s, t, respectively. In this way Kuhn was led to put

$$\omega' = \omega/1{\cdot}5 = 0{\cdot}9333, \qquad \omega'' = \omega/2{\cdot}2 = 0{\cdot}6364 \tag{5}$$

(though different values of ω and ω' were considered by Streitwieser *et al.*[6]). By this means it was hoped that a more adequate allowance had been made for the various inter-electronic Coulomb repulsions.

Kuhn's method has been called the ω''-method. It has been studied by Streitwieser, Heller and Feldman,[6] who attempted to incorporate the terms in ω' and ω'' by an iterative scheme, in which the charges calculated in the n^{th} iteration were used, in (2), to estimate the α-terms for the (n + 1)th iteration. We have thought it desirable to study the ω''-method ourselves, because there are some difficulties associated with the work of Streitwieser *et al.*[6] For example, their iterative scheme seemed often to show divergence, so that it might be thought that the incorporation of ω' and (particularly) ω'' was not possible. In this present paper we first show that, provided a different technique is used, there is no difficulty in getting consistent charges in the ω'- and ω''-methods. We then obtain these charges for three non-alternant hydrocarbons—azulene, fulvene and heptafulvene—and one ion—the benzyl cation. We conclude with a brief discussion of the accuracy of these charges, as judged by the molecular dipole moments to which they lead.

Before leaving this Introduction it may be asked why we have concerned ourselves with variations in the Coulomb terms α_r and not with variations in the resonance integrals β_{rs}, along the lines recently developed by Mulliken and Hoffman.[7,8] It is perfectly true that resonance integrals between other than nearest-neighbour atoms will not vanish. But both they, and the corresponding overlap integrals S_{rs}, will have an exponential type of dependence on the distance between the atoms. Thus, after the first-neighbours these quantities soon become quite small. Coulomb interactions, however, vary as the inverse distance, and therefore act appreciably across quite large separations. It seems possible, therefore, that before including any long-range β_{rs} we ought to include all the terms ω, ω', ω'' . . . In a general discussion of the present kind, however, we shall see that there does not seem to be any point in going beyond ω''.

Self-consistence in the ω''-method

Streitwieser *et al.*[6] have shown, from a study of azulene, that for large ω', the simple iterative method does not converge. We have verified that this holds also when ω'' is included. In the case of the benzyl cation, Streitwieser and Nair[9] have pointed out that even the ω-method itself, without either ω' or ω'', converges very slowly or not at all. Yet the question is a perfectly well-defined one. There must be a definite solution of the following problem: if the Coulomb terms α_r are related to the charges as in (2), what are the values of these charges which lead to α's such that the resulting solutions of the standard secular equations provide the same values of the charges as those originally used to determine the α's?

[6] A. Streitwieser, Jr., A. Heller and M. Feldman, *J. Phys. Chem.* **68**, 1224 (1964).
[7] R. S. Mulliken, *J. Chim. Phys.* **46**, 497 (1949).
[8] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).
[9] A. Streitwieser Jr., and P. M. Nair, *Tetrahedron* **5**, 149 (1959).

We have found two simple ways in which these self-consistent charges may be calculated. Details of these are given in the Appendix. Essentially they depend (1) upon using the arithmetic mean of an even number (two or more) of iterations as starting values for the next iteration, and (2) a quadratic interpolation scheme. No doubt there are other methods. But we have found both of these perfectly straightforward.

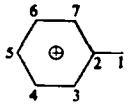


FIG. 1. Benzyl cation

Two examples will show the way in which this convergence is achieved. First, in the case of the benzyl cation (Fig. 1) if we adopt the standard iterative technique of the ω-method, successive net charges on atom 1 are shown in the second row of Table 1. There is no convergence. Next let us start our iteration (Method I) with the arithmetic mean of the first four iterated values in the second row. Thus we take

$$c_1 = \tfrac{1}{4}\{0{\cdot}1697 + 0{\cdot}5697 + 0{\cdot}1532 + 0{\cdot}5879\} = 0{\cdot}3701,$$

as shown in the last row of Table 1. Successive entries in this row now show the results of simple iteration. It is clear that consistency is being achieved, though not very

TABLE 1. CONVERGENCE WITH ARITHMETIC MEAN METHOD FOR BENZYL CATION (ω-MODEL)

Numbers of iterations	0	1	2	3	4	5
Net charge c_1 by standard iterative method	0·5714	0·1697	0·5697	0·1532	0·5879	0·1212
Net charge c_1 by arithmetic mean method (Method I)	0·5714	0·3701	0·3958	0·3726	0·3948	0·3728

rapidly. It could again be speeded up by further use of the arithmetic mean. Finally, in Table 2, we show what happens when the quadratic-convergence method (Method II) is used, including ω' and ω'' terms as well as ω. After nine applications the charges have converged to within 1 in five decimal places. This is shown by the last row which gives the result of a simple interation starting with the previous row. We have found that the benzyl cation was the slowest in convergence of all our molecules; furthermore no one is likely to want anything like this high degree of accuracy. We conclude that there is no essential difficulty in getting self-consistence in any of the ω-type models.

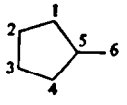
TABLE 2. CONVERGENCE WITH QUADRATIC APPROXIMATION FOR BENZYL CATION (ω''-MODEL)

Net atomic charges	c_1	c_2	c_3, c_7	c_4, c_6	c_5
Hückel values	0·5714	0	0·1429	0	0·1429
Values after 9 cycles of Method II	0·49224	−0·00006	0·08317	0·08544	0·17058
Next iteration	0·49224	−0·00006	0·08317	0·08544	0·17059

Since this work was completed we have seen a paper by Ettinger,[10] who has reached the same conclusions as ourselves when using the arithmetic mean method in order to get convergence. He considered only the ω-method, but showed that, apart from one rather special case, this led to satisfactory convergence in about 36 different molecules. This shows that the topology of the molecule is not significant, and justifies us in believing that the particular values to be reported for the ω'- and ω''-methods are likely to be quite typical. We do not therefore need to consider more than two or three such molecules.

Results in ω-, ω'-, and ω''-methods

Tables 3–5 below show our final calculated self-consistent charges and dipole moments for fulvene, heptafulvene and azulene using both the ω-, ω'- and ω''-approximations, and taking the parameters as in (5). (To facilitate comparisons we have numbered the atoms as in the paper of Streitwieser *et al.*[6]) The headings HMO, ω, ω'



Fulvene

and ω'' for the various columns refer to the Hückel method and its successive refinements. The dipole moments are in Debyes. Most of the ω-values and of the ω'-values are those previously given by Streitwieser *et al.*,[6] but we have verified them*. The ω''-values are believed to be new. The number of iterations required for self-consistency in these calculations was 10 for fulvene, 15 for heptafulvene and 10 for azulene.

TABLE 3. NET CHARGES IN FULVENE

	HMO	ω	ω'	ω''
$c_1(=c_4)$	−0·092	−0·069	−0·080	−0·109
$c_2(=c_3)$	−0·073	−0·041	−0·019	−0·003
c_5	−0·047	−0·021	0·018	0·002
c_6	0·378	0·198	0·181	0·221
μ	4·75	2·7	2·24	2·39

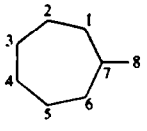


TABLE 4. NET CHARGES IN HEPTAFULVENE

	HMO	ω	ω'	ω''
c_1, c_8	0·058	0·043	0·060	0·075
c_2, c_8	0·038	0·016	−0·006	−0·009
c_3, c_4	0·047	0·029	0·027	0·024
c_7	0·024	−0·024	−0·021	−0·006
c_8	−0·311	−0·154	−0·142	−0·174
μ	4·51	2·5	1·99	2·13

* We are indebted to Dr. H.-D. Försterling for pointing out to us certain errors in the ω-values given by Streitwieser *et al.* for fulvene, heptafulvene and azulene.

[10] R. Ettinger, *Tetrahedron* **20**, 1579 (1964).

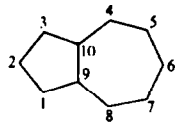


TABLE 5. NET CHARGES IN AZULENE

	HMO	ω	ω'	ω''
c_1, c_3	−0·173	−0·116	−0·115	−0·120
c_2	−0·047	0·045	0·008	0·018
c_4, c_8	0·145	0·093	0·119	0·117
c_5, c_7	0·014	0·023	−0·048	−0·017
c_6	0·130	0·082	0·120	0·059
c_9, c_{10}	−0·027	−0·020	−0·021	−0·018
μ	6·41	4·7	3·25	3·03

These tables show that (i) inclusion of the ω-term usually smooths out the Hückel charges, (ii) further inclusion of ω' smoothes them out a little more, but (iii) the inclusion of ω'' makes relatively little further difference, and may indeed sometimes increase them. These conclusions are shown particularly simply in the dipole moment values. However the dipole moments obtained for fulvene and azulene are always at least twice the observed values ($\sim$1 D.).

This latter situation prompts us to consider the effect of varying ω, ω' and ω''. This has been done for azulene by Streitwieser *et al.*[6,11] insofar as ω and ω' are concerned. We have extended this work to include the ω'' effect. In the first set of calculations we adopted the four sets of values A ... D in the first two columns of Table 6. A comparison of the calculated charges and dipole moments (shown in the other columns of Table 6) confirms that ω'' has very little effect. But the variation of ω' may affect μ by up to 20%.

TABLE 6. NET CHARGES AND DIPOLE MOMENTS FOR AZULENE—VARIOUS ω', ω'' (ω = 1·4)

	ω'	ω''	c_1, c_3	c_2	c_4, c_8	c_5, c_7	c_6	c_9, c_{10}	μ
A	0·467	0·25	−0·113	−0·017	0·100	0·002	0·072	−0·016	3·77
B	0·467	0·40	−0·113	−0·016	0·102	0·004	0·063	−0·016	3·68
C	0·933	0·25	−0·120	0·014	0·113	−0·031	0·094	−0·016	3·21
D	0·933	0·40	−0·120	0·015	0·113	−0·025	0·080	−0·016	3·14

In the second set of calculations we kept ω fixed at 1·4 and ω' at 0·933; and we varied ω''. Table 7 shows the results obtained.

TABLE 7. INFLUENCE OF ω'' ON NET CHARGES AND DIPOLE MOMENT FOR AZULENE

ω''	c_1, c_3	c_2	c_4, c_8	c_5, c_7	c_6	c_9, c_{10}	μ
0	−0·115	0·008	0·119	−0·048	0·120	−0·021	3·25
0·25	−0·120	0·014	0·113	−0·031	0·094	−0·016	3·21
0·40	−0·120	0·015	0·113	−0·025	0·080	−0·016	3·14
0·636	−0·120	0·018	0·117	−0·017	0·059	−0·018	3·03

It is clear from these values that inclusion of ω'' has scarcely any significant effect either on the charges or the dipole moment.

[11] A. Streitwieser, Jr., J. Brauman and J. B. Bush, *Tetrahedron* **19**, Supplement 2, 379 (1963).

CONCLUSIONS

The conclusions from this study are: (i) it is perfectly possible to find self-consistent charges in any of the ω-, ω'- and ω''-models; (ii) the value of ω'' contributes so little to the net charges that it hardly seems justified to include it, in view of the many other assumptions inevitable with any one-electron work of this kind; (iii) with any plausible value of ω the dipole moment is still so far away from experiment that even the inclusion of ω' must be regarded as of doubtful value. In order to reproduce observed dipole moments a totally different ω would be needed, and then the agreement with ionization potentials (on which the choice of ω largely depended) would be destroyed.

It is possible, however, that in the case of charged molecules or radicals, where there are substantial Coulomb-type interactions across fairly large distances, the inclusion of ω' and ω'' may be more significant than for neutral systems where these long-range forces are of much smaller magnitude. Here the best test would be on some of the doubly-ionized molecules such as $C_8H_8^{2-}$ or $C_{10}H_8^{2-}$. With these systems there is no dipole moment to be observed, and so far there are no experimental measurements of bond lengths. Attention would therefore have to be focussed on the ionization potentials. Because of the long-range character of the Coulomb forces, which are now of greater importance, it might well turn out to be necessary to include all orders of ω-type interaction. However, in view of our conclusions about the inadequacy of this method for neutral molecules and radicals, we have not thought it worthwhile to make any such calculations for any doubly-ionized species.

APPENDIX

Methods of obtaining self-consistence

Method I. Let us suppose that for any chosen atom the calculated q at the end of the r'th iteration is $q^{(r)}$. (We drop the suffix denoting which atom it is, to avoid confusion.) Then the usual iterative scheme may be represented by $q^{(r)} \rightarrow \alpha^{(r)}$ using equation (2) $\rightarrow q^{(r+1)}$, from secular equations. This iterative process is continued till convergence is reached (if ever). Often, however, successive $q^{(r)}$ oscillate (see e.g. Table 1). It is then much quicker to start the (r + 1)th iteration with the values

$$\alpha^{(r+1)} = \tfrac{1}{2}\{\alpha^{(r)} + \alpha^{(r-1)}\} \tag{6}$$

This is equivalent to supposing that q is the mean of $q^{(r)}$ and $q^{(r-1)}$. If desired, we could replace (6) by the arithmetic mean of any number of preceding α's, provided only that this number is even.

Method II. This method uses a quadratic interpolation. It may, however, be put graphically as in Fig. 2. In this figure we plot in the (x, y) plane the two points A, C corresponding to

$$(q^{(r-1)}, q^{(r)}) \qquad \text{and} \qquad (q^{(r)}, q^{(r+1)})$$

In words—if we start with $q^{(r-1)}$, the next iteration leads us to $q^{(r)}$ where $q^{(r)}$ is the ordinate of A; and if we start with $q^{(r)}$ the next iteration leads us to $q^{(r+1)}$, which is the ordinate of B. Presumably if we started with some value Q lying between $q^{(r-1)}$ and $q^{(r)}$ we should get to a value represented by the ordinate QB. The simplest approximation to the curve ABC is a straight line; and if the difference $q^{(r)} - q^{(r-1)}$ is not too

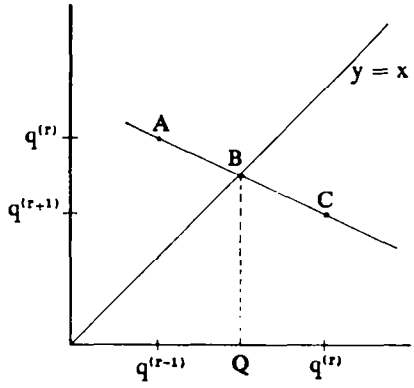


FIG. 2

large, this will be a reasonable representation of the curve. Now if we choose Q, so that, at B, the two coordinates are equal, this will mean that an iteration which starts with the value Q will end with the value Q. To the extent that the curve AC may be replaced by a straight line, this should give the true self-consistent value. If the curve AC is not a straight line we may still expect B to give a close approximation to the self-consistent value.

Analytically B lies on the line AC and also on the line $y = x$. It is straightforward to show that

$$Q = \frac{q^{(r-1)} + \lambda q^{(r)}}{1 + \lambda} \tag{7}$$

where

$$\lambda = \frac{q^{(r)} - q^{(r-1)}}{q^{(r)} - q^{(r+1)}} \tag{8}$$

An equivalent form is due to Dr. M. D. Poole:

$$Q = \frac{\{q^{(r)}\}^2 - q^{(r-1)}q^{(r+1)}}{2q^{(r)} - q^{(r-1)} - q^{(r+1)}} \tag{9}$$

In this method, we use Q rather than $q^{(r+1)}$ as the starting value for the next iteration.

We have found in practice that it is often more convenient to use (7) and (8) separately rather than (9). This is because if the $q^{(r)}$ oscillate, λ is often of the order of $+1$, and there is no loss of accuracy in the use of (7) and (8); but both numerator and denominator in (9) may be sufficiently small that more figures have to be carried throughout in order to avoid losing accuracy.

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