

## Comparisons of the Hückel and Pariser-Parr-Pople-Type MO Methods: Closed Forms for SCF Charge Distributions and Bond Orders\*

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Received May 9, 1966

Analysis of the similarities and differences among the Hückel and Pariser-Parr-Pople-type methods is extended mainly through development for special molecular cases of closed form expressions for the self-consistent wavefunctions. By means of these expressions the various contributions of terms in the Hamiltonian to charge densities, bond orders and other related quantities may be compared term-by-term among the methods. Results on several direct observables, e.g. ionization potentials, electron affinities, bond lengths are similarly dissected. Simplified procedures for generation of the self-consistent charge densities and bond orders from their zeroth-order counterparts in the PPP method are detailed.

Für Moleküle spezieller Symmetrie werden geschlossene Ausdrücke für 'self-consistent'-Wellenfunktionen entwickelt. Aus ihnen lassen sich einfache explizite Reihenentwicklungen für Größen wie Ladungsdichte, Bindungsordnung, Ionisierungsenergie usw. erhalten. Die Verwandtschaft verschiedener MO-Methoden (HMO,  $\omega$ -HMO, PPP) kann so eingehend analysiert werden.

L'analyse des similitudes et des différences entre les méthodes de Hückel et celles du type Pariser-Parr-Pople est élargie essentiellement par l'établissement d'expressions implicites pour les fonctions d'onde self-consistantes dans des cas moléculaires particuliers. A l'aide de ces expressions les contributions des différents termes de l'Hamiltonien aux densités de charges, indices de liaison et autres quantités qui leurs sont liées, peuvent être comparées terme à terme entre les méthodes. Les résultats concernant différentes observables directes comme les potentiels d'ionisation, les affinités électroniques et les longueurs de liaison sont analysés de la même manière. Des procédés simplifiés, qui permettent d'engendrer dans la méthode Pariser-Parr-Pople les densités de charge et les indices de liaison self-consistants à partir des quantités correspondantes à l'ordre zéro, sont exposés.

### 1. Introduction

Inclusion of electron repulsion terms in the Hamiltonian used to compute  $\pi$ -electron wavefunctions for large hydrocarbon molecules has removed important conceptual deficiencies of earlier semi-empirical MO methods. This was the major intention of PARISER and PARR [1] and POPLE [2] who were originally responsible for development of approximations for the repulsion terms. In fact, a balance was sought between incorporation of the most important electron-electron interactions and maintenance of the relative simplicity of wavefunction calculations characteristic of the simpler MO methods. This desire for simplicity was fulfilled, at least for the zeroth-order wavefunctions.

However, since their methods are based upon self-consistent orbital equations [3], the single determinant functions should be made internally self-consistent. It

\* Research performed under the auspices of the U.S. Atomic Energy Commission.

is at this point that the complexity of the calculations, in the sense of the number of arithmetic manipulations necessary, may substantially increase relative to those of simple (Hückel) theory, with which, it seems, improved large molecule-theories are inevitably compared.

It is the purpose of this paper to extend the analysis of differences between the explicit versus averaged electron repulsion Hamiltonian methods, with particular emphasis on how charge distributions are determined and what effects accrue upon imposition of self-consistency procedures. Special molecular cases may be chosen where the S.C.F. procedures typically affect the wavefunctions derived, but where the usual iterative techniques employed may be replaced through analytic summation methods by closed form expressions which yield good approximations to the results obtainable by cycling. From these and the zeroth-order functions for these molecules one may seek a more detailed understanding of how various terms in the Hamiltonian enter the wavefunction computation and ultimately determine various theoretically predicted properties of the molecular state. These results may then be compared, term-by-term, with the Hückel results rather than only as composites and at the end of the calculation\*. Also included where pertinent are the results of an improved version of Hückel theory, i.e. the  $\omega$ -technique, wherein self-consistency procedures are employed and which has been the subject of previous closed form analysis [8].

## 2. Theory

### a) General Features

In the LCAO MO method, the  $i$ -th molecular orbital is expressed in terms of the atomic orbitals,

$$\psi_i = \sum_{\mu} c_{i\mu} \varphi_{\mu}, \quad (1)$$

where the equations which determine the  $\mu$ -th AO coefficients are, under the variational principle,

$$\sum_{\nu} F_{\mu\nu} c_{i\nu} = E_i \sum_{\nu} S_{\mu\nu} c_{i\nu}. \quad (2)$$

Neglecting differential overlap,

$$\sum_{\nu} F_{\mu\nu} c_{i\nu} = E_i c_{i\mu}. \quad (3)$$

In the Pariser-Parr and Pople (PPP) formulations where, in addition to the overlap approximation and the assumption of a constant undeformable  $\sigma$ -core, all electron interaction integrals other than

$$\gamma_{\mu\nu} = \iint [\varphi_{\mu}(1) \varphi_{\nu}(2) \varphi_{\mu}(1) \varphi_{\nu}(2) / r_{12}] dv_1 dv_2$$

are neglected, the pertinent matrix elements become:

$$F_{\mu\mu} = U_{\mu} + \frac{1}{2} q_{\mu} \gamma_{\mu\mu} + \sum_{\nu \neq \mu} (q_{\nu} - 1) \gamma_{\mu\nu}, \quad (4)$$

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\* Several useful reviews of other efforts to explore relations among Hückel theory and a succession of improved theories originating with the Pariser-Parr-Pople methods have recently appeared [4 - 7]. While most of the work cited has been primarily concerned with problems of parameterization in the various methods, some complimentary to that reported here is directed to analysis of the comparative mechanics and toward possible simplifications of the methods.

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \gamma_{\mu\nu}, \quad (5)$$

$$q_{\mu} = \sum_i n_i c_{i\mu}^2, \quad (6)$$

$$p_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}. \quad (7)$$

The zeroth-order elements are computed from the semi-empirical values derived for  $U_{\mu}$ , the electron-core interaction energy,  $\beta_{\mu\nu}$ , the resonance integral which is non-zero only for neighboring, and generally formally  $\sigma$ -bonded sites, and  $\gamma_{\mu\nu}$ , and from the  $q$ 's and  $p$ 's obtained from the Hückel vectors for the pertinent molecule. From these elements, the matrix of Eqs. (3) are solved yielding the first order set of AO coefficients. The latter, in combination with the integral values already used allow computation of a new set of interaction elements, which in turn yield a new set of coefficients. The cycling procedure is continued until the AO coefficients no longer change.

### b) Applications in Special Molecular Cases

In totally symmetric molecules, i.e. those with all AO sites equivalent and with rotational symmetry of the same order as the number of sites, the AO coefficients in each MO are symmetry determined and, hence, by Eqs. (6) and (7), so are the  $q$ 's and  $p$ 's. The self-consistency procedure is therefore convergent in a single cycle and, importantly, by virtue of symmetry demands, the wave function coefficients are identical with those obtained by the Hückel method. In the more interesting cases for our purposes, where all AO sites are not the same, differences in the coefficients will be noted. These differences in turn result in charge density and bond order differences and, hence, in differences in the first- and higher-order energies and associated quantities computed. When we restrict ourselves to molecular cases where two different types of AO sites are present these differences may be followed analytically in much the same manner as they were under the  $\omega$ -technique analysis. Following Ref. [8], we again distinguish between geometric and constitutional AO-site differences and, because of present uncertainties in heteroatom integrals, mainly restrict ourselves to consideration of cases of the former type.

For these cases, the matrix of Eqs. (3) of general order equal to the number of  $\pi$ -AO in the molecule may be reduced by use of symmetry orbital representations to a number of matrices of lower order, each with two blocks centered on the matrix diagonal, representing like-atom interactions, and with off-diagonal blocks for unlike-atom interactions. If advantage is taken of the full symmetry of the like-atom arrangements, matrices of order 2 result\* from transformation of Eqs. (3) to

$$\mathcal{F}_{iAA} C_{iA} + \mathcal{F}_{iAB} C_{iB} = E_i C_{iA}. \quad (8)$$

The  $\mathcal{F}$ -terms arise from the Hamiltonian operating on the symmetry orbitals,  $\chi$ , where  $\chi_A$  and  $\chi_B$  are respectively the orbitals for the sites of types  $A$  and  $B$ ,

\* Having only two types of sites is a necessary but not a sufficient condition for this reduction to order 2 matrices. Apparently, at least for planar molecules, which are of principal concern here, unless the in-plane rotational symmetry is of the same order as the number of individual sites of the more numerous type, matrices of higher order may be unavoidable. Cf. Tab. 1, case II: with the exception of the sub-cases shown which are reducible to order 2, no other molecules meeting the first but not the second condition will be considered.

$$\psi_i = C_{iA} \chi_{iA} + C_{iB} \chi_{iB} = C_{iA} \sum_{j=\text{all } A} a_{ij} \varphi_j + C_{iB} \sum_{k=\text{all } B} b_{ik} \varphi_k, \quad (9)$$

and

$$\int \chi_{iA}^* H \chi_{iA} dv = \mathcal{F}_{iAA}, \quad \int \chi_{iA}^* H \chi_{iB} dv = \mathcal{F}_{iAB}. \quad (10)$$

From Eqs. (8) one may readily show that

$$\bar{E}_{\pm i} = E_{\pm i} - \mathcal{F}_{iAA} = \frac{1}{2} (\Delta_i \pm \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}), \quad (11)$$

$$C_{\pm iA} = C_{\pm iB} \mathcal{F}_{iAB} / \bar{E}_{\pm i}, \quad C_{\pm iB} = [\bar{E}_{\pm i}^2 / (\bar{E}_{\pm i}^2 + \mathcal{F}_{iAB}^2)]^{\frac{1}{2}}, \quad (12)$$

where  $\Delta_i = \mathcal{F}_{iBB} - \mathcal{F}_{iAA}$ , and the  $\pm$  has its usual bonding, antibonding orbital distinction. Since

$$C_{\pm iB}^2 - C_{\pm iA}^2 = \frac{(\bar{E}_{\pm i}^2 - \mathcal{F}_{iAB}^2)}{(\bar{E}_{\pm i}^2 + \mathcal{F}_{iAB}^2)} = \frac{(\Delta_i \pm \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2})^2 - 4 \mathcal{F}_{iAB}^2}{(\Delta_i \pm \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2})^2 + 4 \mathcal{F}_{iAB}^2} = \pm \frac{\Delta_i}{\sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}}, \quad (13)$$

and  $c_{iu}^A = C_{iA} a_{iu}$  for sites of type  $A$  and  $c_{iu}^B = C_{iB} b_{iu}$  for sites of type  $B$ , then the charge density difference components of Eq. (6) may be obtained:

$$(c_{ik}^B)^2 - (c_{ij}^A)^2 = \frac{1}{2} \left\{ \pm \frac{(a_{ij}^2 + b_{ik}^2) \Delta_i}{\sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}} + (b_{ik}^2 - a_{ij}^2) \right\}. \quad (14)$$

The sites  $j$  and  $k$  may be arbitrarily chosen since all sites of a given type will by definition have the same charge density.

In a completely analogous manner the bond order components may be derived:

$$c_{ij}^A c_{ik}^B = a_{ij} b_{ik} \mathcal{F}_{iAB} / \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}, \quad (15)$$

$$c_{ij}^A c_{ik}^A = 2a_{ij} a_{ik} \mathcal{F}_{iAB}^2 / (\Delta_i \pm \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}) (\sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}), \quad (16)$$

$$c_{ij}^B c_{ik}^B = b_{ij} b_{ik} \{1 - [2 \mathcal{F}_{iAB}^2 / (\Delta_i \pm \sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2}) (\sqrt{\Delta_i^2 + 4 \mathcal{F}_{iAB}^2})]\}. \quad (17)$$

Eq. (14) reduces to  $-a_{ij}^2$  if the symmetry orbital function over type  $B$  is nodal at the site  $k$ , and to  $b_{ik}^2$  if the function over type  $A$  is nodal at site  $j$ . Similar straightforward results are obtained for the bond order components in the event of such nodalities.

### c) Linearization of the Charge Density and Bond Order Relations

We will now recognize conditions of apparently wide generality which allow simplification of relations 14 – 17 for the special molecular cases of interest.

In the event that  $|\Delta_i| \ll |2 \mathcal{F}_{iAB}|$ , the square root terms of these equations may be expanded and truncated:

$$(c_{ik}^B)^2 - (c_{ij}^A)^2 = \frac{1}{2} \left\{ (b_{ik}^2 - a_{ij}^2) \pm \frac{a_{ij}^2 + b_{ik}^2}{2 \mathcal{F}_{iAB}} \Delta_i \right\}, \quad (18)$$

$$c_{ij}^A c_{ik}^B = \pm \frac{1}{2} a_{ij} b_{ik} \{1 - (\Delta_i^2 / 8 \mathcal{F}_{iAB}^2)\}, \quad (19)$$

$$c_{ij}^A c_{ik}^A = \frac{1}{2} a_{ij} a_{ik} \{1 \mp (\Delta_i / 2 \mathcal{F}_{iAB})\}, \quad (20)$$

$$c_{ij}^B c_{ik}^B = \frac{1}{2} b_{ij} b_{ik} \{1 \pm (\Delta_i / 2 \mathcal{F}_{iAB})\}. \quad (21)$$

If the changes in  $\Delta_i$  and  $\mathcal{F}_{iAB}$  resulting from cycling are of the same order of magnitude, or if those in the former are greater than in the latter, which, as we shall see, holds generally, then in terms of the small-difference equation

$$\delta X(\Delta_i, \mathcal{F}_{iAB}) = \frac{\partial X}{\partial \Delta_i} \delta(\Delta_i) + \frac{\partial X}{\partial \mathcal{F}_{iAB}} \delta(\mathcal{F}_{iAB}), \quad (22)$$

we find Eqs. (18—21) are, to very good approximations, linear difference equations in the single variable,  $\Delta_i$ . For example, from Eq. (18),

$$\delta[(c_{ik}^B)^2 - (c_{ij}^A)^2] = \pm \frac{a_{ij}^2 + b_{ik}^2}{2} \left\{ \frac{1}{2 \mathcal{F}_{iAB}} \delta(\Delta_i) - \frac{\Delta_i}{2 \mathcal{F}_{iAB}^2} \delta(\mathcal{F}_{iAB}) \right\} \simeq \pm \frac{a_{ij}^2 + b_{ik}^2}{4 \mathcal{F}_{iAB}} \delta(\Delta_i).$$

The difference equation corresponding to Eq. (19), on the other hand, while linear in  $\delta(\Delta_i)$  has a very small coefficient, i.e.  $-\Delta_i/8 \mathcal{F}_{iAB}^2$ , and hence  $c_{ij}^A c_{ik}^B$  is essentially constant upon cycling under these conditions.

In the event  $\Delta_i$  and  $\mathcal{F}_{iAB}$  are of the same order of magnitude but where  $\Delta_i = \eta_i \beta + \bar{\Delta}_i$ , with  $\eta_i \beta$  constant with cycling, and  $|\bar{\Delta}_i| \ll |2 \mathcal{F}_{iAB}|$ , then again expanding and truncating Eqs. (14—17) after the first-power term in  $\bar{\Delta}_i$ ,

$$(c_{ik}^B)^2 - (c_{ij}^A)^2 = \frac{1}{2} \left\{ (b_{ik}^2 - a_{ij}^2) \pm (a_{ij}^2 + b_{ik}^2) \left[ \frac{\eta_i \beta}{X_i^{1/2}} + \frac{4 \mathcal{F}_{iAB}^2}{X_i^{3/2}} \bar{\Delta}_i \right] \right\}, \quad (23)$$

$$c_{ij}^A c_{ik}^B = \pm a_{ij} b_{ik} \frac{\mathcal{F}_{iAB}}{X_i^{1/2}} \left\{ 1 - \frac{\eta_i \beta}{X_i} \bar{\Delta}_i \right\}, \quad (24)$$

$$c_{ij}^A c_{ik}^A = 2a_{ij} a_{ik} \mathcal{F}_{iAB}^2 \left\{ \frac{1}{X_i \pm \eta_i \beta X_i^{1/2}} \mp \frac{\bar{\Delta}_i}{X_i^{3/2}} \right\}, \quad (25)$$

$$c_{ij}^B c_{ik}^B = b_{ij} b_{ik} \left\{ 1 - \frac{2 \mathcal{F}_{iAB}^2}{X_i \pm \eta_i \beta X_i^{1/2}} \pm \frac{2 \mathcal{F}_{iAB}^2}{X_i^{3/2}} \bar{\Delta}_i \right\}. \quad (26)$$

Here,  $X_i = [(\eta_i \beta)^2 + 4 \mathcal{F}_{iAB}^2]$ , and  $\eta_i \beta$  symbolizes intra-type integrals, or sums or differences of such integrals arising from  $\mathcal{F}_{iBB} - \mathcal{F}_{iAA}$ . It should, of course, also be recognized that if  $\eta_i \beta$  is zero, Eqs. (23—26) reduce to Eqs. (18—21), and, moreover, that the former are capable of directly producing the zeroth-order Hückel charge density and bond order components, where  $\mathcal{F}_{iAB}^0 = (\eta_i \beta)^0$  and  $\bar{\Delta}_i^0 = 0$  are the Hückel matrix elements. Again, if the effects of cycling are small and if the changes in  $\bar{\Delta}_i$  are not orders of magnitude smaller than  $\mathcal{F}_{iAB}$ , Eqs. (23—26) are also single variable equations and are linear in the variable  $\bar{\Delta}_i$ . As before  $c_{ij}^A c_{ik}^B$  will be more weakly dependent upon cycling changes in  $\Delta_i$  than the other coefficient terms, here mainly because its  $\bar{\Delta}_i$  coefficient is relatively much smaller. E.g. if  $\eta_i \beta = \mathcal{F}_{iAB}$ , which constitutes a most unusual and unfavorable case, the coefficient of  $\bar{\Delta}_i$  in Eq. (24) will be roughly an order of magnitude smaller than in Eqs. (23), (25) and (26).

#### d) Analytic Linear Interrelations among Charge Density, Bond Order and Components of Energy

Upon consideration of the matrix elements,  $\Delta_i$  and  $\mathcal{F}_{iAB}$ , several important generalizations concerning their nature may be drawn. The former,  $\Delta_i$ , is the difference between interaction elements  $\mathcal{F}_{iBB}$  and  $\mathcal{F}_{iAA}$ , each of which is the combination of  $F_{\mu\mu}$  and  $F_{\nu\nu}$  [Eqs. (4) and (5)] arising from the symmetry orbitals over atoms of type *A* or *B*, where all  $\mu$  and  $\nu$  are either of type *A* or *B*. On the other hand,  $\mathcal{F}_{iAB}$  is the cross-term expressing the interactions between atoms of different types in the different symmetry orbitals; hence, this term will be a combination of  $F_{\mu\nu}$  terms only, where  $\mu$  and  $\nu$  must be *A* and *B*. These generalizations may be expressed symbolically as follows,

$$\Delta_i = F_{BB} - F_{AA} + \sum_{\substack{B, B' \\ B \neq B'}} \tau_{iBB'} F_{BB'} - \sum_{\substack{A, A' \\ A \neq A'}} \tau_{iAA'} F_{AA'}, \quad (27)$$

$$\mathcal{F}_{iAB} = \sum_{A, B} \tau_{iAB} F_{AB}. \quad (28)$$

Note, since the symmetry orbitals are normalized, the coefficients of  $F_{AA}$  and  $F_{BB}$  are unity. From Eqs. (4) and (5), remembering that all sites of the same type have the same charge density and that the  $\tau$ -coefficients are symmetry orbital determined and therefore unchanged upon cycling, we may write,

$$\begin{aligned} \Delta_i &= k + m_B q_B - m_A q_A + \sum \tau_{iBB'} (\beta_{BB'} - \frac{1}{2} p_{BB'} \gamma_{BB'}) - \\ &\quad - \sum \tau_{iAA'} (\beta_{AA'} - \frac{1}{2} p_{AA'} \gamma_{AA'}) \\ &= (\eta_i \beta) + K + M(q_B - q_A) + \sum (T_{iBB'} p_{BB'} - T_{iAA'} p_{AA'}), \end{aligned} \quad (29)$$

$$\mathcal{F}_{iAB} = \sum \tau_{iAB} (\beta_{AB} - \frac{1}{2} p_{AB} \gamma_{AB}) = K'_i + \sum T_{iAB} p_{AB}. \quad (30)$$

The second equality in Eq. (29) is obtained from the first by resolving  $m_B q_B - m_A q_A$  in terms of  $M(q_B - q_A) + k'(n_A q_A + n_B q_B)$  where  $n_A$  and  $n_B$  are the number of sites of the specified types: the latter term is of course constant and known since  $n_A q_A + n_B q_B$  is equal to the total number of  $\pi$ -electrons in the molecule.

Recalling from Eqs. (19) and (24) that  $c_{ij}^A c_{ik}^B$  is higher-order-dependent to cycling changes than the other coefficient product terms, we may assume within our first-order treatment that  $\mathcal{F}_{iAB}$  is constant. Therefore, our earlier assumption of the order of magnitude difference under cycling changes between  $\Delta_i$  and  $\mathcal{F}_{iAB}$  is shown justified, and the following general conclusions may be drawn. The interaction parameters,  $\Delta_i$ , are approximate linear functions, upon cycling, of  $\Delta q$  (i.e.,  $q_B - q_A$ ) and of the bond orders,  $p_{AA'}$  and  $p_{BB'}$ . The latter are, in turn, approximate linear functions of  $\Delta_i$  through the near-linear functionality upon  $\Delta_i$  of their respective components,  $(c_{ik}^B)^2 - (c_{ij}^A)^2$ ,  $c_{ij}^A c_{ik}^A$  and  $c_{ij}^B c_{ik}^B$ . Hence, the following interrelation scheme pertains for the second, the more general, condition outlined above, under the tacit assumption that the expansion-truncation conditions are met in passing from the zeroth- to the first-order coefficient set:

$$\Delta q^t = \Delta q^0 + 2 \sum_i^{\text{occ.}} n_i \{ \pm (a_{ij}^2 + b_{ik}^2) \mathcal{F}_{iAB}^2 / X_i^{3/2} \} \bar{\Delta}_i^t, \quad (31)$$

$$p_{jk}^t(BB') - p_{lm}^t(AA') = \Delta p_{jklm}^0 + 2 \sum_i^{\text{occ.}} n_i \{ \pm (b_{ij} b_{ik} + a_{il} a_{im}) \mathcal{F}_{iAB}^2 / X_i^{3/2} \} \bar{\Delta}_i^t, \quad (32)$$

$$\Delta_i^{t+1} = \eta_i \beta + K + M \Delta q^t + \sum_{A, B} (T_{iBB'} p_{BB'}^t - T_{iAA'} p_{AA'}^t). \quad (33)$$

In these equations, the  $t$ -exponents indicate the cycle number,  $n_i$  signifies the number of electrons in orbital  $i$ , and  $\mathcal{F}_{iAB}$  is constant after the first cycle if  $\eta_i \beta$  is zero or after the second cycle if  $\eta_i \beta$  is non-zero. Natural pairs (or upon occasion when the number of sites of types  $A$  and  $B$  are not the same in the molecule, multiplets) of bond orders exist which allow direct simplification of Eqs. (32) and thereby indirect simplification of Eqs. (33). E.g. for molecules where only constitutional differences exist between site types which are present in equal number, complete pairing may be made where not only are all  $\Delta p^0$  equal to zero, but where  $a_{il} a_{im}$  is equal to  $b_{ij} b_{ik}$  and  $p_{jk}^t(BB') + p_{lm}^t(AA')$  is constant upon cycling. These simplifications may be construed in the following representation of Eqs. (31–33):

$$\Delta p_{jk}^t = \Delta p_{jk}^0 + \sum_i^{\text{occ.}} Y_{ijk} \bar{\Delta}_i^t, \quad (34)$$

$$\Delta_i^{t+1} = K_i + \sum_{jk}^{\text{pairs}} \bar{T}_{ijk} \Delta p_{jk}^t. \quad (35)$$

Here  $\Delta q$  is included as a  $\Delta p$ -term, i.e.  $p_{jj} - p_{ll}$ ; for all, the subscripts  $j$  and  $k$  are given with the natural pairing (with bond order between sites  $l$  and  $m$ ) implicit. The  $\bar{\Delta}_i$ -coefficients of Eqs. (31) and (32) are symbolized as

$$Y_{ijk},$$

$$K_i = K + \eta_i \beta + \sum (T_{ijk} - T_{ilm}) (p_{jk} + p_{lm})/2,$$

$$\bar{T}_{ijk} = (T_{ijk} + T_{ilm})/2.$$

For the cases where more than a constitutional difference exists, or where there are an unequal number of sites, the simplifications will be somewhat different, but the forms of Eqs. (34) and (35) will still pertain. Examination of specific cases, below, will make the choice of pairings and the nature of the simplified coefficients more obvious.

### 3. Change Densities and Bond Orders from Self-Consistent Wavefunctions by Closed-Form Approximation

#### a) Charge Densities: Their Computation and Some Implications to Direct Observables

If Eqs. (34) and (35) are cycled against each other conventionally, the following general relationships are obtained after  $t$ -cycles:

$$\begin{aligned} \Delta p_{jk}^t = & \Delta p_{jk}^0 + \sum_i Y_{ijk} (K_i + \bar{T}_{ijk} \Delta p_{jk}^0) + \\ & + \sum_i Y_{ijk} \left\{ \sum_{j,k} \bar{T}_{ijk} \left[ \sum_i Y_{ijk} (K_i + \bar{T}_{ijk} \Delta p_{jk}^0) \right] \right\} + \dots + \\ & + \sum_i Y_{ijk} \left\{ \sum_{j,k} \bar{T}_{ijk} \left[ \sum_i Y_{ijk} \dots \sum_{j,k} \bar{T}_{ijk} \left( \sum_i Y_{ijk} (K_i + \bar{T}_{ijk} \Delta p_{jk}^0) \right) \dots \right] \right\}, \end{aligned} \quad (36)$$

$$\Delta_i^{t+1} = K_i + \sum_{j,k} \bar{T}_{ijk} \Delta p_{jk}^t. \quad (37)$$

It is quickly apparent that the complex, repeated sums of Eq. (36) are not amenable to direct general solution if more than one  $\Delta p$ -term must be considered. We may, however, take advantage of a corollary of the pair simplification procedure for  $\Delta p$ -terms which allows further simplifications for cycling. The important factors of high symmetry for the molecules of concern and wavefunction nodalities, which provided simpler expressions for  $\Delta p$  than for the individual  $p$ -terms, also provide, upon proper combination, functions of  $\Delta p_{jk}$  which depend strongly on cycling only for certain but not all combinations of  $j$  and  $k$ . Tab. 1—4 contain the cycling equation coefficients for a variety of molecules, both real and hypothetical, which are typical of the cases of present interest and illustrate the ways these combinations may be made.

Tab. 1 displays the constant and change density difference dependence of  $\bar{\Delta}_i$ , terms which are independent of the orbital,  $i$ . In terms of Eq. (35),  $M$  is  $\bar{T}_{i22} = (T_{22} + T_{11})/2$ . One may readily show in general that

$$M = \left\{ n_A \left[ \sum_{\mu=B} (\gamma_{2\mu} - \gamma_{1\mu}) - \frac{1}{2} \gamma_{22} \right] - n_B \left[ \sum_{\mu=A} (\gamma_{2\mu} - \gamma_{1\mu}) + \frac{1}{2} \gamma_{11} \right] \right\} / (n_A + n_B), \quad (38)$$

$$K = (\gamma_{22} - \gamma_{11}) \left\{ 1 - [(n_A q_1 + n_B q_2)/2 (n_A + n_B)] \right\} + \\ + \left\{ 1 - [(n_A q_1 + n_B q_2)/(n_A + n_B)] \right\} \sum_{\substack{\mu=\text{all} \\ \text{sites}}} (\gamma_{1\mu} - \gamma_{2\mu}). \quad (39)$$

In Tab. 2 are the constant intra-site energy terms  $\eta_i \beta$ , and the  $\Delta p$ -terms upon which the  $\bar{A}_i$  depend and which are orbital level dependent. The latter have been grouped to conform to Eq. (35), and their dependencies as expressed in Eq. (34) are displayed in Tab. 3. In Tab. 4, the inter-site ( $AB$ ) interaction energy and bond order relations are given. In all cases where possible, the symmetry orbital representations of the starting wavefunctions were constructed in their imaginary forms, yielding the results, all in real forms, shown in these tables.

It is apparent that in all cases examined here, and seemingly general for all molecules of such high symmetry, the  $\sum T \cdot p$  terms of Eq. (33) are resolvable into  $\Delta p$  and pair- (or multiplet-) sum- $p$  terms, where the latter are zero, and where all remaining  $p$ -terms which are not combinable are found to behave as  $\Delta q$  for the purpose of cycling (cf. the molecules of type II). Moreover, the  $\Delta p$  terms are themselves simple functions of  $\bar{A}_i$ , and because of the wavefunction nodalities which determine their coefficients, *these  $\Delta p$  terms are strongly out of phase with each other*. This latter point which is essential to our ultimate ability to achieve closed forms for cycling may be more specifically illustrated taking the molecules of type I as examples.

For these rings where only a constitutional difference exists between the atoms of type  $A$  and  $B$ , the various  $\Delta p_{2, 2l+2}$  have common dependence upon the sum of quotients,  $\bar{A}_i / \mathcal{F}_i$ , but differ in phase by the factors  $\cos(2\pi il/m)$  applied to each term in the sum. Examination of the sums for the neutral molecules is illuminating:

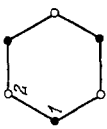
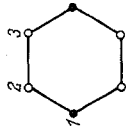
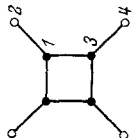
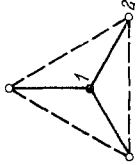
$$\Delta q^{t+1} = m^{-1} \sum_{i=1}^m \bar{A}_i^{t+1} / \mathcal{F}_i \\ = \text{Constant} + M m^{-1} \Delta q^t \sum_i (\mathcal{F}_i)^{-1} - \\ - (4m)^{-1} \sum_{i=1}^{m-1} (\gamma_{2, 2l+2} + \gamma_{1, 2l+1}) \Delta p_{2, 2l+2}^t \sum_i \left( \cos \frac{2\pi il}{m} / \mathcal{F}_i \right) \quad (40)$$

$$\Delta p_{2, 2L+2}^{t+1} = m^{-1} \sum_{i=1}^m \left( \bar{A}_i^{t+1} \cos \frac{2\pi iL}{m} / \mathcal{F}_i \right) \\ = \text{Constant} + M m^{-1} \Delta q^t \sum_i \left( \cos \frac{2\pi iL}{m} / \mathcal{F}_i \right) - \\ - (4m)^{-1} \sum_{i=1}^{m-1} (\gamma_{2, 2l+2} + \gamma_{1, 2l+1}) \Delta p_{2, 2l+2}^t \sum_i \left( \cos \frac{2\pi il}{m} \cos \frac{2\pi iL}{m} / \mathcal{F}_i \right). \quad (41)$$

Here,  $\Delta q$  has been separated from the  $\Delta p$ -terms for clarity; it obviously has the same form with  $L = 0$ , although not an obviously related coefficient. However, upon examination of Tab. 1 and 2, with insertion of numerical values for the contributing  $\gamma$ 's, we conclude that  $|M| > \frac{1}{4} (\gamma_{2, 2l+2} + \gamma_{1, 2l+1})$  generally for any  $l$  and  $m$ , and further, directing our attention to the  $\Delta q$ -equation, that  $|M \sum (\mathcal{F}_i)^{-1}|$  is an order of magnitude greater than  $|4^{-1} (\gamma_{2, 2l+2} + \gamma_{1, 2l+1})|$ .



Table 1. Constant and Charge Density Difference Coefficients for  $\Delta$  in Typical A, B-Containing Molecule Families

Molecule Type	$K - \Delta U - \frac{n_A q_1 + n_B q_2}{2(n_A + n_B)} (\gamma_{22} - \gamma_{11})$	$M - \frac{n_A \gamma_{22} + n_B \gamma_{11}}{2(n_A + n_B)}$
I. Ring, $A_m B_m$ , $m \geq 1$ 	$\frac{q_1 + q_2 - 2}{2} \sum_{l=1}^{m-1} (\gamma_{2,2l+2} - \gamma_{1,2l+1})$	$\frac{1}{2} \left\{ -2\gamma_{12} + \sum_{l=1}^{m-1} (\gamma_{2,2l+2} + \gamma_{1,2l+1} - 2\gamma_{1,2l+2}) \right\}$
II. Ring, $A_m B_{2m}$ , $m = 1, 2^a$ 	$\frac{q_1 + 2q_2 - 3}{3} \sum_{l=1}^{3m-2} (\gamma_{2,l+2} - \gamma_{1,l+2})$	$\frac{1}{3} \left\{ \gamma_{23} - 2(\gamma_{12} + \gamma_{13}) + \sum_{l=1}^{m-1} [\gamma_{2,2l+2} + \gamma_{2,3l+3} - 2(\gamma_{1,3l+2} + \gamma_{1,3l+3} - \gamma_{1,3l+1})] \right\}$
III. Radialenes, $A_m B_m$  $m \geq 2$	$\frac{q_1 + q_2 - 2}{2} \sum_{l=1}^{m-1} (\gamma_{2,2l+2} - \gamma_{1,2l+1})$	$\frac{1}{2} \left\{ -2\gamma_{12} + \sum_{l=1}^{m-1} (\gamma_{2,2l+2} + \gamma_{1,2l+1} - 2\gamma_{1,2l+2}) \right\}$
IV. Axied-Ring, $A B_m$  $m \geq 2$	$\frac{q_1 + m q_2 - (m+1)}{m+1} \left\{ (1-m) \gamma_{12} + \sum_{l=1}^{m-1} \gamma_{2,l+2} \right\}$	$\frac{1}{m+1} \left\{ -2m \gamma_{12} + \sum_{l=1}^{m-1} \gamma_{2,l+2} \right\}$

<sup>a</sup> For  $m > 2$ , cubic equations in  $\Delta$  are generated from symmetry orbital matrices. See footnote page 348 and Ref. [8] part I, Tab. 1.

Table 2. *Intra-Type* (A-A, B-B) Resonance Integral and Bond Order Terms for  $\Delta$ 

Molecule Type	$\eta_{ij}\beta$	$\sum p$ -terms
I.	0	$\frac{1}{4} \sum_{l=1}^{m-1} (\gamma_{1,2l+1} + \gamma_{2,l+2}) (p_{1,2l+1} - p_{2,2l+2}) \cos \frac{2\pi il}{m}$
II. $m = 1$ $m = 2$	$\beta_{23} - \frac{1}{2} p_{23}^0 \gamma_{23}$ $\beta_{23} \cos \pi i - \frac{1}{2} p_{26}^0 \gamma_{26}$	$\frac{1}{2} (p_{23}^0 - p_{23}) \gamma_{23}$ $\frac{1}{8} (p_{14} - p_{23} - p_{25}) (2\gamma_{14} - \gamma_{23} - \gamma_{25}) \cos \pi i + \frac{1}{2} (p_{26}^0 - p_{26}) \gamma_{26}$
III. a b	$\left[ -2\beta_{13} + \frac{1}{4} \sum_{l=1}^{m-1} (\gamma_{1,2l+1} + \gamma_{2,2l+2}) (p_{1,2l+1}^0 - p_{2,2l+2}^0) \cos \frac{2\pi il}{m} \right]$	$\frac{1}{4} \sum_{l=1}^{m-1} (\gamma_{1,2l+1} + \gamma_{2,2l+2}) (\Delta p_{1,2l+1} - \Delta p_{2,2l+2}) \cos \frac{2\pi il}{m}$
IV. a b c	$(2\beta_{23} - \frac{1}{2} \sum_{l=1}^{m-1} p_{2,l+2}^0 \gamma_{2,l+2}) \cos \frac{2\pi il}{m}$	$\frac{1}{2} \sum_{l=1}^{m-1} \Delta p_{2,l+2} \gamma_{2,l+2} \cos \frac{2\pi il}{m}$

<sup>a</sup> When  $m = 2$ , the  $\beta$  coefficients must be reduced by one-half.

<sup>b</sup>  $\Delta p \equiv (p^0 - p)$ .

<sup>c</sup> Generally, only the  $i = m$  MO will enter the  $\Delta q$ - and  $p$ -relations, since all other MO's normally occupied are nodal in site 1 (A).

Table 3. Dependence of Charge Density and Bond Order Upon Terms in  $\Delta^a$ 

Molecule Type	$\Delta q = q_B - q_A$	Bond Order Relations
I.	$\frac{1}{m} \sum_{i=1}^m \bar{\Delta}_i$	$p_{1,2i+1} - p_{2,2i+2} = -\frac{1}{m} \sum_{i=1}^m \frac{\bar{\Delta}_i}{\mathcal{F}_i} \cos \frac{2\pi il}{m}$ $p_{1,2i+1} + p_{2,2i+2} = 0$
II.	$\Delta_+ = 3(G - 1 + H\bar{\Delta})/4$ $\Delta_- = 3(G + H\bar{\Delta})/2$ $3H(\bar{\Delta}_1 + \bar{\Delta}_2)/4$	$p_{33}^{(+)} = (G + 3 + H\bar{\Delta})/4$ $p_{23}^{(-)} = (G + H\bar{\Delta})/2$ $p_{23} + p_{25} - p_{24} = 1 + (p_{25} - p_{23} - 2p_{14}) = 2G + H(\bar{\Delta}_2 - \bar{\Delta}_1)$ $p_{23} + p_{25} + p_{14} = 0; \quad p_{26} = H(\bar{\Delta}_1 + \bar{\Delta}_2)/2$
III.	$\frac{2}{m} \sum_{i=1}^m (G_i + H_i \bar{\Delta}_i)$	$p_{1,2i+1} - p_{2,2i+2} = -\frac{2}{m} \sum_{i=1}^m (G_i + H_i \bar{\Delta}_i) \cos \frac{2\pi il}{m}$ $p_{1,2i+1} + p_{2,2i+2} = 0$
IV. <sup>b</sup>	$\frac{1}{m} \left\{ G_m + H_m \bar{\Delta}_m \right\}$	$p_{2,i+2} = \bar{p}_{2,i+2} + \frac{1}{m} \left\{ G_m - 1 + H_m \bar{\Delta}_m \right\}$

<sup>a</sup>  $G_i = \eta_i \beta [(\eta_i \beta)^2 + 4\mathcal{F}_i^2]^{1/2}$ ,  $H_i = 4\mathcal{F}_i^2 / [(\eta_i \beta)^2 + 4\mathcal{F}_i^2]^{1/2}$ .<sup>b</sup>  $p_{2,i+2}$  is the pertinent bond order for the mono-anion of the isolated ring.

Table 4. Closed Form Expressions for  $\mathcal{F}_{iAB}$  and  $p_{AB}$

Molecule Type	$\mathcal{F}_{iAB}$	$p_{AB}$
I.	$\sum_{l=1}^m F_{1,2l} \cos \frac{\pi i(2l-1)}{m}$ $i = 1, 2, \dots, \frac{m-1}{2} \text{ or, } \frac{m}{2} \text{ and } m$ $\mathcal{F}_{m-i} = \mathcal{F}_i$	$p_{1,2i} = \begin{cases} \frac{\sin \pi (2l-1)/2}{m \sin \pi (2l-1)/2m}, & m \text{ odd} \\ \frac{\sin \pi (2l-1)/2}{m \tan \pi (2l-1)/2m}, & m \text{ even} \end{cases}$
II. $m = 1$	$\sqrt{2} F_{12}$	$p_{12} = a F_{12}^2 / V(\eta_t \beta)^2 + 8 F_{12}^2, (A = \pm, a = 1, 2)$
$m = 2$	$\sqrt{2} (F_{12} + F_{13} \cos \pi i)$	$p_{11} = \frac{1}{\sqrt{2}} \sum_{i=1}^2 (-1)^{i+1} \mathcal{F}_i V(\eta_t \beta)^2 + 4(\mathcal{F}_i)^2$
III.	$\sum_{l=1}^m F_{1,2l} \cos \frac{2\pi i(l-1)}{m}$	$p_{1,2i} = \frac{2}{m} \sum_{i=1}^m \frac{\mathcal{F}_i \cos \frac{2\pi i(l-1)}{m}}{V(\eta_t \beta)^2 + 4(\mathcal{F}_i)^2}$
IV.	$\sqrt{m} F_{1,2}$	$p_{12} = \frac{2F_{12}^2}{V(\eta_t \beta)^2 + 4mF_{12}^2}$

$\cdot \sum \cos \frac{2\pi il}{m} |\mathcal{F}_i|$ . This implies that the major dependence of  $\Delta q$  upon cycling is on  $\Delta q$  itself, with only secondary mixing of the various bond-order difference terms.

Therefore, to a fair approximation,

$$\Delta q^{t+1} = \text{Constant} + \{Mm^{-1} \sum (\mathcal{F}_i)^{-1}\} \Delta q^t. \quad (42)$$

More specifically,

$$\Delta q^0 = \frac{A_0}{2\beta} \cdot \frac{1}{m} \sum_{i=1}^m \left| \cos^{-1} \frac{\pi i}{m} \right|, \quad (43)$$

where  $A_0$  is the Hückel Coulomb integral difference,  $\alpha_Y - \alpha_X$ .

$$\Delta q^{t+1} = \frac{1}{m} \sum_{i=1}^m \frac{K + M\Delta q^t}{(\mathcal{F}_i)} = \frac{K + M\Delta q^t}{m} \sum_{i=1}^m (\mathcal{F}_i)^{-1} \quad (44)$$

for all  $t$ , and  $\mathcal{F}_i$  is unchanged upon iteration after cycle 1 (*vide supra*). We may obtain the next higher order to improve our approximation without changing the form of Eq. (44) by recognizing that the  $\Delta p$ 's will be subject to variations upon cycling which are on the same order or smaller than those in  $\Delta q$ . Hence, an effective  $M$  ( $M'$ ) may be defined which incorporates the bond order contributions for the first cycle as a good approximation to the bond order contributions to all following cycles. I.e.,

$$\begin{aligned} \frac{K + M'\Delta q^0}{m} \sum_i (\mathcal{F}_i)^{-1} &= \frac{K + M\Delta q^0}{m} \sum_i (\mathcal{F}_i)^{-1} - \\ &- (4m)^{-1} \sum_l (\gamma_{2, 2l+2} + \gamma_{1, 2l+1}) \Delta p_{2, 2l+2}^0 \sum_i \left( \cos \frac{2\pi il}{m} \right) |\mathcal{F}_i|. \end{aligned} \quad (45)$$

Symbolizing  $m^{-1} \sum (\mathcal{F}_i)^{-1}$  as  $A$ , it is immediately apparent that  $\Delta q$  is a geometric progression with initial (Hückel) parameter residues,

$$\Delta q^{t+1} = \frac{K}{M'} \left[ \sum_{j=1}^{t+1} (AM')^j \right] + (AM')^{t+1} A_0 A_0. \quad (46)$$

For  $|AM'| < 1$ , the converged value for  $\Delta q$  is

$$\Delta q^\infty = KA/(1 - AM'). \quad (47)$$

$A_0$  is of course  $(2\beta m)^{-1} \sum \left| \cos^{-1} \frac{\pi i}{m} \right|$ . In a similar manner self-consistent bond order relations may be generated (*vide infra*).

Tab. 5 displays some test results for the ring,  $m = 5$ , with  $A_0$  and  $K$  both chosen as 0.1 eV. These and the other parameter values shown in the Table conform fairly closely to the POPLE values for hydrocarbons [2] and may be thought of as being representative of a ten-membered planar hydrocarbon ring with alternative atoms substituted by some weak purely inductive groups. The Hückel- $\omega$ -technique results are included for comparison. These results directly indicate several important procedural points and as well suggest some possible generalizations concerning the PPP method and contrasts with methods where averaged repulsions are employed.

The electron interactions responsible for the negative value of  $M$  are instrumental in increasing the charge disparity over that predicted by the zeroth-order Hückel Hamiltonian, i.e.  $-0.04762$  vs.  $-0.04161$ . The value of  $\Delta q$  continues to

increase upon approach to the self consistent orbitals, with the  $\Delta q^\infty$  roughly 40% greater than the first-order result.

Completely ignoring the effects of the bond order terms one obtains results which noticeably underestimate the strength of the repulsions, although the correct qualitative behavior is predicted. By increasing the value of  $M$  by about 10%, as prescribed above for  $M'$ , the first- and subsequent higher-order results are reproduced essentially quantitatively. While it does not seem possible to generalize about the relative size of  $M$ -corrections, it does seem likely that such corrections will be possible based upon the first order results and that they generally will be smaller than the original  $M$  itself due to phase considerations.

Table 5. *Charge Density Differences for Molecular Case I,*  
 $m = 5$ , with  $\Delta_0 = 0.1$  eV

Cycle No.	Eq. 38 <sup>a</sup>	Eq. 42 ( $M = -3.9$ ) <sup>b</sup>	$\Delta q^t$ ( $M' = -4.3_3$ )	Hückel- $\omega^c$
0	-0.04161	-0.04161	-0.04161	-0.04161
1	-0.04762	-0.04459	-0.04762	+0.01032
2	-0.05211	-0.04656	-0.05205	-0.05449
3	-0.05552	-0.04787	-0.05531	
4	-0.05813	-0.04874	-0.05774	
.				
.				
.				
$\infty$	-0.0665 <sup>d</sup>	-0.0505 <sup>e</sup>	-0.0644	-0.0185 <sup>f</sup>

<sup>a</sup> All terms; essentially identical with results obtainable by conventional cycling of the secular equations.

<sup>b</sup>  $M = (\gamma_{11} + \gamma_{22})/4 - 2\gamma_{12} + 2\gamma_{13} - 2\gamma_{14} + 2\gamma_{15} - \gamma_{16} = 5.26 - 14.60 + 10.40 - 9.20 + 7.80 - 3.5$  in eV.

<sup>c</sup>  $\Delta^{t+1} = \Delta_0 - \omega\beta^0\Delta q^t$ ;  $\Delta q^t = (2m\beta^0)^{-1} \Delta^t \sum_{i=1}^m \left| \cos^{-1} \frac{\pi i}{m} \right|$ ;  $-\omega\beta^0 = +3.0$  eV.

<sup>d</sup> Average from geometric extrapolations using points 1, 2 and 3 and points 2, 3, 4. The difference between results from these two sets is 0.0004.

<sup>e</sup> From Eq. 45.

<sup>f</sup> Back-extrapolation of divergent results, cf., Ref. [8], part II, Eq. 9.

On the other hand, the  $\omega$ -technique, wherein electron repulsions are supposedly averaged, predicts a decrease of the original charge disparity upon attainment of self-consistent orbitals. This is generally the result of this method and arises from the positive value for  $-\omega\beta^0$ , contrasted to the negative value of  $M$  [cf., footnote c of Tab. 5 and, in contrast, Eq. (42)]. The fact that conventional cycling produces divergence is a mechanical result; the  $\Delta q_{\text{Hückel}}^\infty$  and  $\Delta_{\text{Hückel}}^\infty$  values reported (the latter is 0.0445 eV) correspond to self-consistent orbitals for this system and hence are appropriate for our comparisons.

It is apparent from examination of Eq. (38) which contains the general expression for  $M$  for the two-site type systems, as well as of footnote b of Tab. 5, that  $M$  will be negative as long as the sum of repulsion terms between unlike sites is greater than the sum of such terms between like sites. A negative value of  $M$  as we have just seen will result in an increase rather than a diminution in  $\Delta q$ , neglecting the relatively smaller effects of the  $\Delta p$  terms. The important questions which

are posed therefore are, under what circumstances will  $M$  be negative, and how for the cases where it is negative can the  $\omega$ -technique which operates with what is essentially a positive  $M$  be reconciled.

It is quite clear that  $M$  will be negative as long as unlike sites are on the average geometrically closer to each other than are like sites in the pertinent molecules. This requirement must be somewhat strengthened in that the self-repulsion term, i.e.  $(\gamma_{11} + \gamma_{22})/4$ , must be overcome by the difference between unlike and like site interactions between non-identical sites. Clearly, in the cases we have chosen, which are representative of two type site molecules and include many real molecular systems, negative  $M$  values will occur more often than not. Only in the relatively few cases where like sites are formally bound to each other or where unusual geometries pertain, may we expect the average like-site distances to be as close or closer than unlike-site distances and hence produce a positive  $M$ . Therefore, although quantitative generalizations to molecules with more than two types of sites are not possible in that  $M$  loses its distinct meaning, we must conclude that, at the very weakest,  $M$  may be of either sign for physically realizable molecules. This implies a definite disagreement with the precept of the  $\omega$ -technique which assigns a positive coefficient to the dependence of  $\Delta$  on charge density difference independent of molecular structure [8].

The origin of this disagreement may easily be traced. That  $\omega$  should not only have a positive value (to make  $-\omega\beta^0$  positive), but a sizable one at that, could be semi-empirically justified by approximating the Coulomb integral of a free  $sp^2$  carbon atom by the average of the ionization potential and electron affinity. One then relates the Coulomb integral change presumably undergone by this atom to the  $\Delta q$  change accompanying ionization of its  $p$ -electron through the basic  $\omega$ -technique equation [9],

$$\begin{aligned} -\frac{1}{2} [I (C_{sp^2}^0) + A (C_{sp^2}^0)] + \frac{1}{2} [I (C_{sp^2}^+) + A (C_{sp^2}^+)] &\simeq 12 \text{ eV} \\ &= (\alpha_{C^+} - \alpha_{C^0}) = \omega\beta^0(q_0 - q_+) = \omega\beta^0. \end{aligned}$$

This approximation for the atom yielded a value of  $\sim 5$  for  $\omega$  which was known to overestimate charge redistribution effects in molecular systems and more often than not to cause divergences in the cycling scheme (values of  $\sim 1$  appeared empirically to be more satisfactory). It was quite reasonably assumed that other atoms bonded to the site of ionization would buffer the gross Coulomb integral change and hence lower the value of  $\omega$ .

The buffer effect exercised by donation of electrons to shield the charge deficient site must be of a short range nature if a single value of  $\omega$  is to apply to hydrocarbon molecules generally. On this basis and to avoid introducing redundancies in the  $\pi$ -electron calculation, most of the shielding effects must be postulated to arise from the  $\sigma$ -framework, i.e., to be  $\pi$ -induced  $\sigma$ -effects. Quite obviously, since molecular geometries vary so widely, it is impossible for an average of  $\pi$ -induced  $\pi$ -effects, either in the sense of donation of shielding electrons or in electron repulsions to appreciably contribute to  $\omega$ . We must conclude therefore, in light of the excellent success the  $\omega$ -technique has in correlation of conjugated hydrocarbon ionization potentials, that the Hückel method itself must be capable of averaging much of the  $\pi$ -effects upon certain molecular properties, but that there is no justification in assuming any direct correspondence between inclusion of repulsion

terms in the Hamiltonian and  $\omega$ -technique applications in their absence. This conclusion agrees with a similar deduction obtained from purely numerical results on ionization potentials previously [8].

To follow the consequences of the preceding arguments a bit further, it is of interest to note that the energy changes in the  $\sigma$ -framework attendant upon the short range shielding of a  $\pi$ -charge deficient site could very well be constant or essentially so, in accord with the constant lowering of the free atom  $\omega$  over all molecules of concern, and hence to be incorporable in the  $\alpha^0$  term in the ionization energy. The value of  $\alpha^0_+$  found empirically in the ionization correlation is  $-9.88$  eV, compared to  $-7.2$  eV for  $\alpha_C$  for free  $sp^2$  C [10], or an effect of  $-2.68$  eV. If we make the assumption that the deshielding effect in the electron affinity process is of the same size,  $\alpha^0_-$  would be  $-4.52$  eV, and the heretofore uncorrelated electron affinities of hydrocarbon molecules now are quite well fitted by  $\bar{A} = -\alpha^0_- - \left(m_{\bar{N}} - \frac{\eta+1}{\eta}\omega\right)\beta^0$ . See Eq. (24) of Ref. [8 (part I)] and Tab. 3 therein, and Tab. 6 here where the deshielding effect is included. It is of further interest to note that

Table 6. *Electron Affinities of Hydrocarbon Molecules in eV*

Molecule	$\omega = 1.4$ $\alpha^0_- = -4.52$ eV	Pople	Experimental
Ethylene	-2.02	-1.81	
Benzene	-1.04	-1.40	-0.54
Butadiene	-0.48	-0.34	
Allyl Radical	+0.58	+0.24	+2.1
Benzyl Radical	+1.14	+0.69	+1.8
Styrene	-0.20	-0.29	
Methyl Radical	-1.99	-1.03	+1.1
Triphenylmethyl	+1.35	+1.65	+2.1
Biphenyl	-0.44	-0.37	+0.41
Naphthalene	-0.04	-0.14	+0.65
Phenanthrene	+0.08	-0.06	+0.69
Anthracene	+0.48	+0.64	+1.19

now  $\bar{I} + \bar{A} = -(\alpha^0_+ + \alpha^0_-) + 2\omega\beta^0 = 8.49$  eV, constant for all hydrocarbon and substituted hydrocarbon molecules where the theoretical method applies, and in excellent agreement with the value of 8.47 obtained in the Pople method [11].

The foregoing discussion brings us most naturally to an examination of the performance of the explicit electron repulsion method under similar circumstances. The Pople method is known to yield satisfactory correlations of ionization potentials for alternant hydrocarbon molecules and is felt to be, in the absence of a comparable body of experimental results, similarly reliable for electron affinities. However, the method as generally applied invokes Koopman's Theorem; when the energy difference is taken between the two states, both optimized with respect to the S.C.F. conditions, the results are rather poorer. We may therefore conclude that this method as generally applied also does some interaction averaging, most of which is probably incorporated in the  $U$ 's, the electron-core interaction energy, a term which contributes to the energy difference only in processes where the number of electrons changes.



A further and perhaps more striking insight into the differences predicted by the explicit *vs.* averaged electron repulsion methods for charge density, is to be found upon consideration of molecules having structural branch points or tertiary sites. These are sites which are bound to three other conjugating sites in the molecule. Where the  $\omega$ -technique, in its usual manner, predicts levelling of the charge density differences arising from the zeroth-order Hückel MO's, in the PPP method greater charge density is often computed for these tertiary sites in the carbonium ions than in the neutral parent molecules [2]. Analogously, less density is found at these sites in the carbanions than in the neutral parents. These apparently anomalous results arise from a combination of two factors which may be precisely examined for case IV,  $m = 3$ ; extensions to both the hypothetical higher branched molecules and to molecules with more than two types of sites are easily visualized from the results of this case. In accord with our earlier observation concerning geometric proximity of unlike *versus* like sites in the molecule,  $M$  is negative for this molecule. From Tab. 1,

$$2m\gamma_{12} > \left( \frac{\gamma_{22} + m\gamma_{11}}{2(m+1)} + \sum_{l=1}^{m-1} \gamma_{2,l+2} \right),$$

independent of whether the peripheral groups are formally bonded or not. (So are the general conclusions independent of this bonding, although the quantitative results will differ.) Hence, the PPP method will predict a greater charge disparity than will the Hückel method for the perturbed neutral molecule.

In the carbonium ion whose peripheral groups are not bonded to each other, because the highest filled MO is nodal at the tertiary site numbered as 1 in Tab. 1, the Hückel MO's predict  $\Delta q_+^0 = -1/3$  (or  $-1/m$  for other number of branches). The complete closed form calculation proceeds as follows.

Here, because only one MO is not nodal at the branch site, a single  $\Delta$  pertains:

$$\begin{aligned} \Delta_+^{t+1} &= K + M\Delta q_+^t - \frac{1}{2}(2) p_{23}^t + \gamma_{23}, \\ \Delta q_+^t &= -\frac{1}{3} + \left(\frac{4}{3}\right) \Delta_+^t / 2 \mathcal{F}_{12} = -\frac{1}{3} + 2\Delta_+^t / 3 \sqrt{3} F_{12} = B + A\Delta_+^t, \\ \Delta p_{23+}^t &= \frac{1}{6} + \left(\frac{1}{3}\right) \Delta_+^t / 2 \mathcal{F}_{12} = \frac{1}{6} + \Delta_+^t / 6 \sqrt{3} F_{12} = \frac{1}{4}(\Delta q_+^t + 1), \\ F_{12} &= \beta_{12} - \frac{1}{2} p_{12} \gamma_{12}, \quad p_{12} = \frac{1}{\sqrt{3}}. \end{aligned}$$

It should be noted that  $\Delta p$  is linearly related to  $\Delta q$  here; hence  $M'$  will represent an exact rather than approximate cycling variable:

$$\begin{aligned} \Delta_+^{t+1} &= K' + M' \Delta q_+^t, \\ M' &= M - \gamma_{23}/4 = \gamma_{11}/2 + [-6\gamma_{12} + 2\gamma_{23}]/4 - \gamma_{23}/4, \\ K' &= K - \gamma_{23}/4 = -[-2\gamma_{12} + 2\gamma_{23}]/4 - \gamma_{23}/4. \end{aligned}$$

Noting that all internal angles in this molecular are  $120^\circ$ , assuming benzene bond lengths and by recourse as above to the summation of geometric progressions,

$$\Delta q_+^\infty = \frac{B + K'A}{1 - M'A} = \frac{-1/3 + (-0.445 \text{ eV}) (-0.856 \text{ eV}^{-1})}{1 - (-4.32 \text{ eV}) (-0.0856 \text{ eV}^{-1})} = -0.4685.$$

Therefore, with inclusion of the  $\omega$ -technique values ( $\omega = 1.4$ ):

Hückel	$q_{1+}^0 = 1.0000,$	$q_{2+}^0 = 0.6667 ;$
PPP	$q_{1+}^\infty = 1.0814,$	$q_{2+}^\infty = 0.6329 ;$
$\omega$ -tech.	$q_{1+}^\infty = 0.9125,$	$q_{2+}^\infty = 0.6958 .$

It is now apparent why the branch site exhibits excess charge density in the carbonium ion in the PPP method. Not only is  $M$  (more correctly  $M'$ ) negative which enhances the zeroth-order charge density difference, but because the branch site is nodal in the MO from which the ionization occurs, the zeroth-order density for this site is unaffected by the ionization. Hence, since a unit charge exists before electron repulsion operates to increase this density,  $q_{1+}$  must be larger than one. It might be mentioned that this anomaly could be mitigated in some cases if  $K$  (or  $K'$ ) were large enough to decrease the zeroth-order density difference which appears in the numerator of the final  $\Delta q_{\pm}^{\infty}$  expression — here it is roughly 3-times too small. Moreover, we may conclude that branch sites are not necessary to affect such a charge pile-up; as long as a site is nodal or near-nodal in the ionization-MO and  $M'$  is negative, the same result may be obtained. For example, in the allyl radical,  $q_{1+}^{\infty} = 1.065$ ,  $q_{2+}^{\infty} = 0.467$ . Conversely, we may conclude that if the tertiary site in a molecule is not nodal in the highest filled MO of a neutral molecule, or if  $M'$  is not negative, or if  $K'$  is sufficiently large, then  $\pi$ -charge build-up may not be predicted in the carbonium ion.

*b) Self-Consistent Bond Orders from Closed Form Expressions*

The trans-butadiene molecule provides a good example for demonstration of the term-by-term analysis of bond order effects possible with the closed form self-consistency expressions developed here. The case is of particular interest in that intimate comparisons may easily be drawn with the corresponding results of the Hückel and  $\omega$ -technique-type methods which are known to overestimate the central bond order and hence to underestimate the corresponding bond length. This particular failure has been assumed symptomatic, and rightly so, of the inability of the averaged repulsion methods, parametrized for other observables, to correlate  $\pi$ -electronic effects on molecular structure.

Trans-butadiene is a case III member with  $m = 2$ :

$$\begin{aligned}\bar{A}_j^{t+1} &= M\Delta q^t + N_j\Delta p^t, \\ N_j &= \frac{1}{4}(\gamma_{13} + \gamma_{24})\cos\pi j, \\ \Delta p^t &= (p_{13} - p_{24})^t - (p_{13} - p_{24})^0 = \Delta p^t - \Delta p^0, \\ \eta_j\beta &= [-\beta_{13} + \frac{1}{4}(\gamma_{13} + \gamma_{24})\Delta p^0]\cos\pi j, \\ \mathcal{F}_{j12} &= F_{12} + F_{14}\cos\pi j.\end{aligned}$$

Since  $F_{14} = -\frac{1}{2}p_{14}\gamma_{14}$  and  $p_{14} = 0$ , then

$$\begin{aligned}\mathcal{F}_{112} &= \mathcal{F}_{212} = \mathcal{F}, \\ G_1 &= -G_2 = \eta_1\beta/[(\eta_1\beta)^2 + 4(\mathcal{F})^2]^{\frac{1}{2}}, \\ H_1 &= H_2 = 4(\mathcal{F})^2/[(\eta_1\beta)^2 + 4(\mathcal{F})^2]^{\frac{3}{2}}.\end{aligned}$$

Further, since  $\Delta q^0 = 0$ , we observe that  $\bar{A}_1^1 = -\bar{A}_2^1$  and

$$\Delta q^1 = H_1\bar{A}_1^1 + H_2\bar{A}_2^1 = H(\bar{A}_1 + \bar{A}_2) = 0.$$

Hence, inductively,  $\bar{A}_1^t = -\bar{A}_2^t$  and  $\Delta q^t = 0$ . Therefore

$$\Delta p^t = G_1 + H_1\bar{A}_1 - G_2 - H_2\bar{A}_2 = 2(G_1 + H_1\bar{A}_1).$$

We observe then that  $\Delta p^1 = 2G_1$ , and by summation of the geometric progressions involving  $\Delta p^t$  and  $\bar{\Delta}_1^{t+1}$ ,

$$\Delta p^\infty = \frac{2G_1 - 2HN_1 \Delta p^0}{1 - 2HN_1} = \frac{\Delta p^1 - 2HN_1 \Delta p^0}{1 - 2HN_1}.$$

Recalling that  $p_{13}^t + p_{24}^t = 0$  we can extract  $p_{13}$  at any stage, i.e.,  $p_{13}^\infty = \frac{1}{2} \Delta p^\infty$ .

The value so obtained is essentially a static self-consistent field result, i.e., the bond order corresponding to the fixed geometry assumed for the carbon atoms in butadiene. The first two row-blocks of Tab. 7 show the results obtained for  $p_{13}$  and  $p_{12}$  and associated quantities assuming the molecule has equal bond lengths of

Table 7. Bond Orders and Associated Quantities for *trans*-Butadiene<sup>a</sup>

Method	footnote	$p_{12}$	$p_{12}^\infty$	$p_{13}$	$p_{13}^\infty$	$2HN_1$	$\mathcal{F}$ (eV)	$\bar{\Delta}_1^\infty$ (eV)
static, bonds equal	} <sup>b</sup>	0.911	0.911	0.398	0.366	0.383	-5.655	
		0.911	0.919	0.394	0.361	0.381	-5.715	0.48
			0.933	0.389	0.354	0.378	-5.796	
static, short-long alternation	} <sup>d</sup>	0.937	0.940	0.342	0.280	0.373	-6.116	0.92
			0.962	0.337	0.274	0.369	-6.209	
dynamic	<sup>c e</sup>	0.930	0.960	0.351	0.278	0.432	-6.240	1.05
Hückel, static		0.894	0.894	0.447	0.447			
Hückel, dynamic	<sup>f</sup>	0.918	0.922	0.395	0.387	0.116	$1.082\beta^0$	$-0.02\beta^0$

<sup>a</sup> The first three sets of results are from the closed form PPP relations, the last two are from the Hückel and modified Hückel methods.

<sup>b</sup> Assuming  $\mathcal{F}$  is converged after a single cycle; the second row result is obtained with the second cycle result for  $\mathcal{F}$ .

<sup>c</sup> Obtained by correcting  $p_{12} = p_{12}(1 - [\eta_{11}\beta/(\eta_{11}\beta)^2 + 4\mathcal{F}^2]\bar{\Delta}_1^\infty)$  and recycling to obtain the new  $(p_{13} - p_{24})$ .

<sup>d</sup>  $\gamma_{12} = 7.5$  eV,  $\gamma_{13} = 7.1$  eV and  $\gamma_{24} = 3.9$  eV;  $\beta_{12} = -2.6$  eV and  $\beta_{13} = -2.1$  eV.

<sup>e</sup> Starting with bonds equal and assuming  $\beta = \beta^0 S/S^0 = \beta^0(0.195 + 0.08 p)/S^0$ , and  $\gamma(\text{neighbors}) = 7.30(1 + 1.40(0.09)(p - 2/3))$ , the latter by assumption of reciprocal dependence of  $p$  upon  $r$  and fitting parameters to benzene and ethylene distances. While these are somewhat cruder than currently prescribed variation methods [7, 6, 12], they provide the desired linear  $p$ -dependence. Note as well,  $\gamma_{24}$  is assumed constant in the dynamical calculations since  $r_{24}$  is essentially independent of the degree of bond alternation.

<sup>f</sup> Assuming the same dependence of  $\beta$  upon  $p$  as in footnote <sup>e</sup>.

benzene length ( $\beta = -2.39$  eV) and also assuming the terminal bonds are shorter and the central bond longer so as to correspond to  $\beta_{12} = -2.6$  and  $\beta_{13} = -2.1$  eV.

The results obtained employing equal bond lengths and short-long alternation in the static case show significant differences. We observe that a central bond order of 0.274 is obtained when alternation is assumed compared to 0.354 when all bonds are held at the benzene bond length. The former is roughly 40% smaller than the zeroth-order Hückel result while the latter shows only about half this diminution.

In contrast to these static results, one may obtain a set of truly self-consistent results, within the limitations of the method, by obtaining dependences of the resonance and repulsion integrals upon internuclear distance and thence upon bond orders through semi-empirical relations among these quantities. The linear semi-empirical relations employed are detailed in the footnotes to Tab. 7 and were obtained by Taylor expansions about first-order static results previously obtained.

What this dynamical procedure does operationally is merely to change the linear parametric dependence of  $p_{12}$  upon  $\mathcal{F}$  and *vice versa*, and of  $\Delta p_{13}$  upon  $\bar{\Delta}$  and  $\mathcal{F}$ . The most important differences from the static results are detectable upon examination of  $2HN_1$  and the incomplete alternation predicted by the Hückel zeroth-order results themselves. Note the closed form expressions are not altered between the static and dynamic methods.

We find that the dynamic self-consistent procedure starting at the equal bond length configuration can produce  $p_{12}^\infty$  and  $p_{13}^\infty$  values which are in good agreement with previous electron repulsion included calculations on butadiene [3, 13] and very close to the alternant short-long static system previously examined. Further, and most important, these results are essentially independent of the starting configurations; only in the event of such a distorted initial configuration so as to invalidate the Taylor expansions will this independence not apply. The final dynamical result is partly due to the first cycle correction which already recognizes considerable alternation through diminution of  $\eta_1\beta$  and a simultaneous increase of  $\mathcal{F}$ , and partly to the comparatively large self-consistency factor  $2HN_1$ . The latter, in turn is large because the linear coefficient relating  $\bar{\Delta}$  to  $\Delta Ap$ , which is  $(\gamma_{13} + \gamma_{24})/4$ , is enhanced by the  $\beta$  and  $\gamma_{13}$  dependences upon  $\Delta Ap$ ; i.e.,  $N_1$  which is 2.8 eV in the static systems is 3.29 eV when the  $\beta$  and  $\gamma$  variational dependences are included.

By much the same token, the dynamical Hückel results can not produce the same degree of alternation, principally because of the weak proportionality of  $\bar{\Delta}$  upon  $\Delta Ap$  arising from the lack of repulsion terms in the proportionality constant. The entire dependence falls upon the  $\beta$ -upon- $p$  linear factor, which is the same incidentally as that employed in the previous calculations but which constitutes only of the order of 10–20% of the total value of  $N_1$  in those calculations\*. The Hückel value for  $2HN_1$  is seen consequently to be only about  $\frac{1}{3}$ – $\frac{1}{4}$  the size of the corresponding factors in the electron repulsion cases. The difference between the methods is further emphasized by examination of the  $\bar{\Delta}_1$  values, which are in essence orbital energy differences between the external and internal sites in the butadiene molecule. When electron repulsion effects are included  $\bar{\Delta}_1$  is about 1 eV, contrasted to about 0.05 eV when these terms are neglected or averaged for the individual sites. As a final comparison, it is of interest to compute the bond lengths corresponding to the converged bond orders obtained by the various methods using the reciprocal relationship employed in the dynamical calculations,  $1/r = 0.6557_6 + 0.0916_2 p$ . The results, all in Ångstroms, are for the PPP method,  $r_{12} = 1.34_5$ ,  $r_{13} = 1.46_8$ ; from the self-consistent Hückel method,  $r_{12} = 1.35_1$  and  $r_{13} = 1.44_6$ . The value of  $r_{13}$  from the zeroth-order results in  $1.43_5$ .

It is quite apparent from scrutiny of this example why the Hückel method as applied cannot produce the same effects upon cycling as can the repulsion-included methods. There is no direct means within the former to recognize the geometric differences which exist among molecules with regards to such features as terminal sites, multiplicity of bonding to any given site, etc. Such features can obviously be

\* MULLIKEN and co-workers many years ago computed somewhat greater alternation by this method but only upon assumption of considerably steeper dependence (roughly twice) of  $\beta$  upon  $r$  and hence upon  $\Delta p$  [14].

of varying importance depending upon the molecular property examined. Differences in success of parametrization must also be expected in the simple theory depending upon the molecular property.

It does not seem unreasonable then to expect that properties which are directly dependent upon the cycling variables, such as charge densities, bond orders and site-site polarizations would be more sensitive to these geometric factors than less direct quantities such as ionization potentials, resonance energies and spectral transition energies. The latter are considered indirect only in the sense that they are properties of the entire molecule in more than one state rather than of individual sites in a given state. By the same token, it is not surprising that we are better able to parametrize the Hückel method for energy differences than for electron distributions. Conversely, we must expect that correct predictions for the latter might require either somewhat better detailed methods of averaging, e.g. geometric dependence for  $\omega$ , or parametrization at a different stage in the calculations. Fixing  $\beta$  and its relationship to intersite distances for bond order computations alone, without regard to the different relationships which may hold for correlation of other observables is an example of the latter procedure.

Finally, we may conclude, accepting the electron repulsion included methods as more precisely representative of the bond order-bond length conditions which exist in alternant hydrocarbons, that the charge densities computed by the Hückel method are less reliable than those forthcoming from the repulsion included methods, and, that when a substantial difference exists between the results of the different methods, those of the latter be more readily but by no means completely authoritatively accepted.

### *c) Concurrent Charge Density and Bond Order Effects in Closed Form*

As a final illustrative example of the possible range of utility for the closed form expressions developed here, we may examine the quantum chemical MO representation of a recently synthesized member of the radialene family, trimethylenecyclopropane [15]. This molecule is of case III, with  $m = 3$ . We recognize that this is not an alternant hydrocarbon, and, since the obvious strain which exists in the ring and as well the hybridization of these sites is not fully accounted for, suggest that the results be taken with the proper degree of scepticism that such simplifications merit.

Assuming all bond lengths equal and  $1.40 \text{ \AA}$  ( $\beta_{12} = \beta_{13} = -2.39 \text{ eV}$ ), then  $\Delta q^0 = 0.1249$ ,  $\Delta p^0 = (p_{13}^0 - p_{24}^0) = 0.7695$ ,  $p_{12}^0 = 0.8320$  and  $p_{14}^0 = -0.0624$ . With  $\gamma_{24}$  computed as  $3.76 \text{ eV}$  from the unit point charge approximation [2] and  $\gamma_{14} = 4.90 \cdot 2/1.932 = 5.07 \text{ eV}$ , we find  $M = -1.1_2 \text{ eV}$ . The first order results are  $\Delta q = 0.0553$ ,  $\Delta p = 0.6912$ ,  $p_{12} = 0.8677$ ,  $p_{14} = -0.0593$  and the rapidly convergent closed form expressions yield  $\Delta q = 0.0561$  and  $\Delta p = 0.685$ . An  $M'$  of  $\sim -0.6$  is found to reproduce these values, with neglect of sizable  $\Delta \Delta p = (p_{13} - p_{24} - p_{13}^0 + p_{24}^0)$ , again because of phase averaging compensations over the  $\bar{A}_j$ 's.

These results indicate a preference for charge to concentrate slightly in the terminal atoms, i.e.  $q_2 = 1.028$  and  $q_1 = 0.972$ . The molecule should also exhibit distinct short and long bonds respectively in the branches and in the ring ( $p_{12} =$

= 0.868 and  $p_{13} = 0.342$ )<sup>\*</sup>, although no excessive trust should be put in the quantitative results since we here have only obtained the static results corresponding to initial assumption of equivalent bond lengths. It appears that the dynamic method would result in a further decrease of the charge density difference and an increase in the degree of short-long bond alternation. The concentration of charge, it should further be noted, is determined mainly by the non-alternant nature of the molecule (viz.,  $\Delta q^0$ ), with a distinct amelioration due to the electron repulsion effects exercised in terms of a decrease in the  $G$ -values, and also, less importantly, in a negative  $M$ . Again we encounter  $M$  as negative; in this case, however, the self-consistency procedure is seen to parallel that which would be obtained in the  $\omega$ -technique which, as we have seen, apparently always works to smooth charge distribution irregularities.

Perhaps the most important additional point which may be gleaned from study of this example is in illustration of the apparent general efficacy of approximating the coefficient of particular  $\Delta p$  in the same manner as an effective  $M$  ( $M'$ ) could be approximated for  $\Delta q$ . This coefficient could then be utilized in development of closed form relations for  $\Delta p$ .

From Eq. (41), in analogy to the development in Eqs. (42–46),

$$\begin{aligned} \Delta p_{2,2L+2}^{t+1} = & \text{Constant} + Mm^{-1} \Delta q^t \sum_i \left( \cos \frac{2\pi iL}{m} | \mathcal{F}_i \right) - (4m)^{-1} \sum_{\substack{l=1 \\ l \neq L}}^{m-1} (\gamma_{2,2l+2} + \\ & + \gamma_{1,2l+1}) \Delta p_{2,2l+2}^t \sum_i \left( \cos \frac{2\pi i}{m} \cos \frac{2\pi iL}{m} | \mathcal{F}_i \right) \\ & - (4m)^{-1} (\gamma_{2,2L+2} + \gamma_{1,2L+1}) \Delta p_{2,2L+2}^t \sum_i \left( \cos^2 \frac{2\pi iL}{m} | \mathcal{F}_i \right). \end{aligned} \quad (48)$$

Upon recognition of the partial phase cancellation over  $i$  for the  $\Delta q$  term and over land  $i$  for the separated bond order terms, we obtain:

$$\Delta \Delta p_{2,2L+2}^\infty = \Delta p_{2,2L+2}^\infty - \text{Constant} = KB_L / (1 - B_L N').$$

Here, in straightforward analogy to Eq. (47),  $B_L$  is  $-m^{-1} \sum \cos^2(2\pi iL/m) | \mathcal{F}_i$  and  $N'$  is the  $\Delta \Delta p_{2,2L+2}^t$  coefficient obtained by averaging so as to produce the same result for  $\Delta \Delta p_{2,2L+2}^{(2)}$  as was obtained in Eq. (48) which is exact, i.e.,

$$N' = \Delta \Delta p_{2,2L+2}^{(2)} (\text{exact}) / B_L \cdot \Delta \Delta p_{2,2L+2}^{(1)} (\text{exact}).$$

In the present example, there is only a single bond order difference to consider (i.e.  $p_{13} - p_{24}$ ). Hence,  $N'$  will have only to incorporate the  $\Delta q$  term. It is of interest to note then that while the exact  $N = (\gamma_{13} + \gamma_{24})/2$  is 5.53 eV,  $N'$  is 4.8 eV and  $\Delta p^{(3)}$  (exact) is 0.6841, while  $\Delta p^{(3)}$  obtained using  $N'$  is 0.6840. As was reported previously, a value of  $M' \sim -0.6$  eV could reproduce the  $\Delta q$  values obtained by conventional cycling with  $M = -1.1$  eV and upon retention of the  $\Delta p$ -term.

#### d) Extensions of the Formalism

While major emphasis has been placed here on the computation and comparison of charge densities and bond orders, the relations exist in Eqs. (11), (29) and

\* The bond lengths corresponding to these bond orders are by the reciprocal  $r$ - $p$  relationship previously employed,  $r_{12} = 1.36$  Å and  $r_{13} = 1.46$  Å. Conventionally cycled PPP method results are 1.35 and 1.46 Å respectively [16].

(30) to compute the orbital energies for the special molecular cases, and through the self-consistent wavefunctions themselves other expectation values. Further simplifications of the closed form expressions and extensions to other than the special molecular cases for some of these quantities are presently being sought. These efforts are directed along the lines followed for ionization potentials and electron affinities in the  $\omega$ -technique analysis previously described.

### References

- [1] PARISER, R., and R. G. PARR: *J. chem. Physics* **21**, 466, 767 (1953).
- [2] POPLE, J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953); *J. physic. Chem.* **61**, 6 (1957).
- [3] ROOHTAAN, C. C. J.: *Rev. mod. Physics* **23**, 61 (1951).
- [4] LYKOS, P. G.: *Advances in Quantum Chemistry* **1**, 171 (1964).
- [5] I'HAYA, Y.: *Advances in Quantum Chemistry* **1**, 203 (1964).
- [6] FISCHER-HJALMARS, I.: *Molecular Orbitals in Physics, Chemistry and Biology*, LöWDIN, P. O., and B. PULLMAN, Eds., p. 361. New York: Academic Press 1964; *Theoret. chim. Acta* **4**, 332 (1966).
- [7] MCWEENY, R.: *Molecular Orbitals in Physics, Chemistry and Biology*, LöWDIN, P. O., and B. PULLMAN, Eds., p. 305. New York: Academic Press 1964.
- [8] EHRENSON, S.: *J. physic. Chem.* **66**, 706, 712 (1962).
- [9] MULLER, N., L. W. PICKETT, and R. S. MULLIKEN: *J. Amer. chem. Soc.* **76**, 4770 (1954).
- [10] I'HAYA, Y.: *J. chem. Physics* **23**, 1165 (1955).
- [11] BRICKSTOCK, A., and J. A. POPLE: *Trans. Faraday Soc.* **50**, 901 (1954).
- [12] NISHIMOTO, K., and N. MATAGA: *Z. physik. Chem. [Frankfurt]* **12**, 335 (1957).
- [13] MULLIKEN, R. S.: *Tetrahedron* **6**, 68 (1959).
- [14] —, C. A. RIECKE, and W. G. BROWN: *J. Amer. chem. Soc.* **63**, 41 (1941).
- [15] DORKO, E. A.: *J. Amer. chem. Soc.* **87**, 5518 (1965).
- [16] DEWAR, M. J. S., and G. J. GLEICHER: *J. Amer. chem. Soc.* **87**, 692 (1965).

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