

207. *Structure and Properties of Mesomeric Systems. Part III.* Charge Distribution and Related Properties in Non-alternant Hydrocarbons.*

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A perturbation method is used to obtain the charge distribution in some of the larger cyclic non-alternant hydrocarbons. Several properties related to charge distribution are discussed.

In Part II,* perturbation methods were used to study the chemical reactivity of the larger non-alternant hydrocarbons. Atom localisation energies for ionic and free-radical reaction have been obtained in a simple manner, thus eliminating the excessive labour involved in the conventional procedure. We now examine charge distribution in the ground state of mesomeric hydrocarbons, a property which is important in itself and also in several applications. In alternant hydrocarbons, the charge distribution is, in the Hückel approximation, uniform throughout the ring, the charge on each carbon atom being unity.¹ In the non-alternant hydrocarbons, however, there is an uneven charge distribution^{1,2,3} but its formal calculation is tedious and a perturbation method by which it may be obtained is now described.

The approach to be adopted follows from the work of Coulson and Longuet-Higgins⁴ and of Dewar and Pettit.⁵ The former authors have developed a series of polarisabilities, the one of interest here being the atom-bond polarisability $\pi_{t,rs}$:

$$\pi_{t,rs} = \delta q_t / \delta \beta_{rs} = 4 \sum_{p=1}^m \sum_{q=m+1}^n [c_{tp}c_{tq}(c_{sp}c_{rq} + c_{sq}c_{rp}) / (e_p - e_q)] \dots \dots (1)$$

* Part II, preceding paper.

¹ Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.

² Brown, *Trans. Faraday Soc.*, 1948, **44**, 984; 1949, **45**, 296.

³ Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85**, 929.

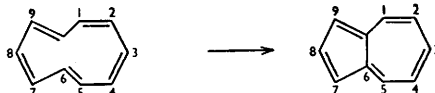
⁴ Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; 1947, *A*, **192**, 16.

⁵ Dewar and Pettit, *J.*, 1954, 1617.

This quantity describes the change (δq_t) in the charge on atom t resulting from a change ($\delta\beta_{rs}$) in the resonance integral of the bond between atoms r and s . The bonding molecular orbitals are $1 - m$, the antibonding $(m + 1) - n$; the c 's are atomic-orbital coefficients of self-evident nomenclature and e_q and e_p are the energies of the q th and p th molecular orbitals.

Dewar and Pettit⁵ have used the analogous bond-bond polarisability $\pi_{st,uv}$ to estimate the effect on the bond orders of the peripheral bonds of the formation of the cross-links in the benzenoid hydrocarbons.

We wish to know what will be the effect on the charge on the other carbon atoms of the formation of such cross-links. As an example, we regard azulene as being derived from cyclodecapentaene by the formation of the cross link (the numbering used is not the usual chemical numbering):



and the polarisability $\pi_{1,6:10}$ will give an estimate of the change in the charge on carbon atom 1 resulting from the formation of the 6 : 10 cross-link. The charge on all carbon atoms of the parent cyclic polyene is, of course, unity.

Now Coulson and Longuet-Higgins show⁴ that the degeneracy of all but the highest antibonding and the lowest bonding molecular orbitals of the cyclic polyene necessitates our using the correct zeroth-order wave functions (ψ) for the degenerate levels: *

$$\left. \begin{aligned} \psi_j(\cos) &= \chi_j \sum_{a=1}^n \cos \left(2aj \frac{\pi}{n} + \epsilon_j \right) \phi_a \\ \psi_j(\sin) &= \chi_j \sum_{a=1}^n \sin \left(2aj \frac{\pi}{n} + \epsilon_j \right) \phi_a \end{aligned} \right\} \dots \dots \dots (2)$$

Rather different treatments are required for the $(4\gamma + 2)$ and the (4γ) cycles and the former class is dealt with first.

The $(4\gamma + 2)$ Hydrocarbons.—The nomenclature of eqn. (1) being modified slightly for the cyclic polyenes, the occupied molecular orbitals are $0-\gamma$, the unoccupied $(\gamma + 1)-(2\gamma + 1)$ and eqn. (1) becomes

$$\pi_{t,rs} = 4 \sum_{j=0}^{\gamma} \sum_{k=\gamma+1}^{2\gamma+1} [c_{tj}c_{rk}(c_{sj}c_{rk} + c_{rj}c_{sk}) / (e_j - e_k)] \dots \dots \dots (3)$$

In this equation, the first summation is to be taken over all the bonding, the second over all the antibonding, orbitals and for each value of j and k there are two orbitals having cosine and sine wave functions (2).

Reduction of equation (3) gives (Appendix 1)

$$\pi_{t,rs} = 4 \sum_{j=0}^{\gamma} \sum_{k=\gamma+1}^{2\gamma+1} \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \left\{ \cos 2(t-r)k \frac{\pi}{n} \cdot \cos 2(t-s)j \frac{\pi}{n} \right. \\ \left. + \cos 2(t-r)j \frac{\pi}{n} \cdot \cos 2(t-s)k \frac{\pi}{n} \right\} \dots \dots (4)$$

The disappearance of ϵ is a useful result, the practical significance being that the numbering of the cyclic polyene is arbitrary. Further reduction (Appendix 2) gives

$$\pi_{t,rs} = 2 \left[\cos(t-r)\pi + \cos(t-s)\pi \right] \left[\sum_{j=0}^{\gamma} \frac{\chi_j^4}{e_j} \left\{ \cos 2(t-s)j \frac{\pi}{n} \cdot \cos 2(t-r)j \frac{\pi}{n} \right\} \right. \\ \left. + 2 \sum_{j=0}^{\gamma-1} \sum_{h=j+1}^{\gamma} \frac{\chi_j^2 \cdot \chi_h^2}{(e_j + e_h)} \left\{ \cos 2(t-r)j \frac{\pi}{n} \cdot \cos 2(t-s)h \frac{\pi}{n} + \cos 2(t-s)j \frac{\pi}{n} \cos 2(t-r)h \frac{\pi}{n} \right\} \right] \dots \dots (5)$$

* The energy levels and the wave functions of a cyclic polyene and the phase factor ϵ are described in the preceding paper. Symbols common to both papers are as defined there.

Now in certain cases—when ε° is zero, for example—the numerator vanishes for all values of e_p and e_q and so, by assumption, the term is zero when e_p and e_q are zero. When cross-links are formed between atoms of like parity only, ε° is zero and ρ is zero. When cross-links are formed between atoms of opposite parity only, $(r + s)$ is odd and $2\varepsilon^\circ$ is often $\pm\pi/2$ and ρ vanishes again. The term becomes indeterminate when ε° assumes an intermediate value. In what follows, it is assumed that ρ is zero but it must be emphasised that the conclusions are only valid when this is the case.

The polarisability $\pi_{t,rs'}$ does not refer to the cyclic polyene itself, in which the non-bonding molecular orbitals are both singly occupied, but to the artificial state in which one of these orbitals is doubly occupied and the other is empty. The charge distribution is not uniform in the latter state and the charge (δq_t°) resulting from this electron reorganisation must be added to $\delta q_t'$ to produce the total charge (q_t) of the t th carbon atom of the cross-linked hydrocarbon. It is easily shown that

$$\delta q_t^\circ = \pm \frac{2}{n} \left[\cos^2 \left(\frac{t\pi}{2} + \varepsilon^\circ \right) - \sin^2 \left(\frac{t\pi}{2} + \varepsilon^\circ \right) \right] = \pm \frac{2}{n} \cos(t\pi + 2\varepsilon^\circ) \quad (11)$$

the plus sign being taken when the cosine wave function is doubly occupied and the minus sign when the sine wave function is doubly occupied. The total charge (q_t) resulting from the formation of one cross-link is given by

$$(q_t - 1) = \pi_{t,rs'} \cdot \beta + \delta q_t^\circ \quad (12)$$

$$= 4 \sum_k^{\text{occ.}} \sum_l^{\text{unocc.}} [c_{rj}c_{lk}(c_{sj}c_{sk} + c_{sj}c_{rk}) / (e_j - e_k)] \pm \frac{2}{n} \cos(t\pi + 2\varepsilon^\circ) \quad (13)$$

and reduction of the first term on the right-hand side of eqn. (13) gives (Appendix 3)

$$\begin{aligned} (q_t - 1) = & 2 \left[\cos(t-r)\pi + \cos(t-s)\pi \right] \left\{ \sum_{j=0}^{\gamma-1} \left[\frac{\chi_j^4}{e_j} \cdot \cos 2(t-s)j\frac{\pi}{n} \cdot \cos 2(t-r)j\frac{\pi}{n} \right] \right. \\ & + 2 \sum_{j=0}^{\gamma-2} \sum_{h=j+1}^{\gamma-1} \frac{\chi_j^2 \cdot \chi_h^2}{(e_j + e_h)} \left[\cos 2(t-r)j\frac{\pi}{n} \cdot \cos 2(t-s)h\frac{\pi}{n} + \cos 2(t-s)j\frac{\pi}{n} \cos 2(t-r)h\frac{\pi}{n} \right] \left. \right\} \\ & + 4 \left[\sin \left(\frac{t\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(\frac{s\pi}{2} + \varepsilon^\circ \right) + \cos \left(\frac{t\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(\frac{s\pi}{2} + \varepsilon^\circ \right) \cdot \cos(t-r)\pi \right] \times \\ & \left[\sum_{j=0}^{\gamma-1} \frac{\chi_j^2 \cdot \chi_j^2}{e_j} \cos 2(t-r)j\frac{\pi}{n} \right] \\ & + 4 \left[\sin \left(\frac{t\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(\frac{r\pi}{2} + \varepsilon^\circ \right) + \cos \left(\frac{t\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(\frac{r\pi}{2} + \varepsilon^\circ \right) \cdot \cos(t-s)\pi \right] \times \\ & \left[\sum_{j=0}^{\gamma-1} \frac{\chi_j^2 \cdot \chi_j^2}{e_j} \cos 2(t-s)j\frac{\pi}{n} \right] \\ & \pm \frac{2}{n} \cos(t\pi + 2\varepsilon^\circ) \quad (14) \end{aligned}$$

In eqn. (14), it has been assumed that the cosine wave function non-bonding molecular orbital is doubly occupied and the sine wave function non-bonding molecular orbital is unoccupied. If the converse is the case, the equation must be modified slightly as shown in Appendix (3).

From eqns. (5) and (14) we can calculate the charge distribution of all of the $(4\gamma + 2)$ non-alternant hydrocarbons and of some of the (4γ) representatives. Formal calculations of the charge distribution of the simpler non-alternant hydrocarbons have been reported^{1,2,3} and these results $[10^3(1 - q_i)]$ are compared (inner numerals) in Fig. 1 with

FIG. 1.

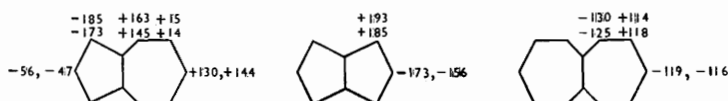
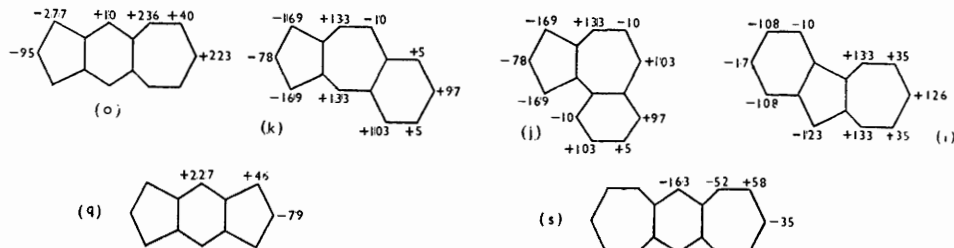


FIG. 2.



the results of the perturbation method (outer numerals). To illustrate the use of the latter technique, the charge distribution of some of the larger non-alternant hydrocarbon has been calculated and the results $[10^3(1 - q_i)]$ are reported in Fig. 2. For convenience, aromatic bonds are omitted.

DISCUSSION

Comparison of the perturbation charge distribution and the exact figures, where the latter are available (Fig. 1), shows that the perturbation method reproduces the sign and the magnitude of the charges with very encouraging accuracy. A more extensive comparison is precluded by the scarcity of formal calculations and this shortage emphasises the great amount of labour involved in the complete treatment.

Using the perturbation method, we can examine the charge distribution of the larger non-alternant hydrocarbons (Fig. 2). Linear benzinterposition has little effect on the orientation of charge in azulene, pentalene, or heptalene, but the sizes of the charges are substantially altered, those in azulene being increased, those in pentalene and heptalene being reduced. Benzannulation has a relatively small effect on the charge distribution of azulene, both the orientation and the sizes of the charges remaining almost unchanged. The perturbation method is not generally applicable to the benzannulated pentalenes and heptalenes. As is discussed below, there is a good parallel between the charges and the ionic localisation energies of these hydrocarbons.

Charge distribution plays an important part in several properties of mesomeric systems.⁷ The most direct result of an uneven charge distribution is the existence, in an unsymmetrical hydrocarbon, of a dipole moment, but in this application, some refinement of the simple Hückel method is required to obtain results of more than qualitative significance (cf. ref. 7, chap. 7). For this reason, the subject is not examined further now.

Charge distribution is fundamental to one of the two molecular-orbital theories of chemical reactivity—the isolated-molecule approximation.⁸ In this approach, it is supposed that the carbon atom having the greatest surplus of positive or negative charge in the ground state will be the preferred position of attack by nucleophils and electrophils,

⁶ Hückel, *Z. Physik*, 1930, **60**, 423; 1931, **70**, 204; 1931, **72**, 310; 1932, **76**, 628.

⁷ Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952.

⁸ R. D. Brown, *Quart. Rev.*, 1952, **6**, 63.

respectively. While this assumption is probably less sound than the localisation method used in the preceding paper, it is interesting to compare the results from both sources. Such comparison shows that there is good qualitative agreement as to the most reactive position for ionic substitution in all of the hydrocarbons studied. This agreement strongly reinforces our confidence in the perturbation methods. For example, both methods predict that benzinterposition will not change the orientation of ionic substitution in the odd-numbered rings of azulene, pentalene and heptalene and that it will increase the ionic reactivity of azulene but decrease that of pentalene and heptalene. Quantitatively, the agreement is not exact, but this situation is not confined to the results of the perturbation method, the two approaches giving slightly different results in the exact treatment for the azulene molecule.

Another property in which charge distribution is of importance is the basicity of the derived azaheterocycle. Suppose that a carbon atom of a mesomeric hydrocarbon is replaced by a nitrogen atom. Longuet-Higgins has shown⁹ that the basicity of the azaheterocycles is related to the charge (q_t) at this carbon atom (t) in the parent hydrocarbon by the equation:

$$2.3RT \cdot pK_a = \text{constant} - q_t \delta \alpha_t \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $\delta \alpha_t$ is the change in the Coulomb integral of the nitrogen atom on protonation. Since $\delta \alpha$ is negative here, the greater the charge on atom t of the parent hydrocarbon, the greater the basicity of the azaheterocycle. In fact, a graph of the pK_a 's against q_t should give a straight line having a positive slope. Longuet-Higgins shows⁹ that this result is approximately true for a number of compounds. Since we can now obtain the charge distribution of many of the larger non-alternant hydrocarbons, it is simple to predict the basicities of the derived azaheterocycles. A few compounds of this type have been reported recently¹⁰ but there seem to be no data by which the perturbation method can be tested.

APPENDIX I

It is required to obtain equation (4) from equation (3). We have

$$\pi_{t,rs} = 4 \sum_{j=0}^{\gamma} \sum_{k=\gamma+1}^{2\gamma+1} [c_{ij}c_{ik}(c_{sj}c_{rk} + c_{sk}c_{rj})/(e_j - e_k)] \quad . \quad . \quad . \quad (3)$$

Consider one bonding pair of degenerate molecular orbitals (j) and one antibonding degenerate pair (k), the respective phase factors being ϵ_j and ϵ_k . The single term arising from the bonding cosine wave function [$\psi_j(\cos)$] and the antibonding cosine wave function [$\psi_k(\cos)$] is

$$4 \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \cos \left(2tj \frac{\pi}{n} + \epsilon_j \right) \cdot \cos \left(2tk \frac{\pi}{n} + \epsilon_k \right) \left[\cos \left(2sj \frac{\pi}{n} + \epsilon_j \right) \cdot \cos \left(2rk \frac{\pi}{n} + \epsilon_k \right) + \cos \left(2rj \frac{\pi}{n} + \epsilon_j \right) \cdot \cos \left(2sk \frac{\pi}{n} + \epsilon_k \right) \right] \quad . \quad . \quad (16)$$

and there is another term from the same bonding cosine wave function orbital [$\psi_j(\cos)$] and the antibonding sine wave function [$\psi_k(\sin)$]:

$$4 \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \left[\cos \left(2tj \frac{\pi}{n} + \epsilon_j \right) \cdot \sin \left(2tk \frac{\pi}{n} + \epsilon_k \right) \left[\cos \left(2sj \frac{\pi}{n} + \epsilon_j \right) \cdot \sin \left(2rk \frac{\pi}{n} + \epsilon_k \right) + \cos \left(2rj \frac{\pi}{n} + \epsilon_j \right) \cdot \sin \left(2sk \frac{\pi}{n} + \epsilon_k \right) \right] \quad . \quad . \quad (17)$$

⁹ Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

¹⁰ Treibs, *Annalen*, 1952, **576**, 110; Treibs, Steinert, and Kirchhof, *ibid.*, 1953, **581**, 54; Anderson and Tazuma, *J. Amer. Chem. Soc.*, 1952, **74**, 3455; Nozoe, Mukai, and Murata, *ibid.*, 1954, **76**, 3352; Lloyd, *Chem. and Ind.*, 1953, 921; Hunter, Lloyd, Marshall, Price, and Rowe, *ibid.*, 1954, 1068.

Multiplying out (16) and (17), and summing, we have:

$$4 \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \left[\cos \left(2tj \frac{\pi}{n} + \epsilon_j \right) \cdot \cos \left(2sj \frac{\pi}{n} + \epsilon_j \right) \cos 2(t-4)k \frac{\pi}{n} + \right. \\ \left. \cos \left(2tj \frac{\pi}{n} + \epsilon_j \right) \cos \left(2rj \frac{\pi}{n} + \epsilon_j \right) \cos 2(t-s)k \frac{\pi}{n} \right] \quad . \quad . \quad (18)$$

Another pair of terms arises from the bonding sine wave function orbital [$\psi_j(\sin)$] and the antibonding cosine and sine wave function orbitals [$\psi_k(\cos)$ and $\psi_k(\sin)$]. Summing as before, we have

$$4 \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \left[\sin \left(2tj \frac{\pi}{n} + \epsilon_j \right) \sin \left(2sj \frac{\pi}{n} + \epsilon_j \right) \cdot \cos 2(t-r)k \frac{\pi}{n} + \right. \\ \left. \sin \left(2tj \frac{\pi}{n} + \epsilon_j \right) \cdot \sin \left(2rj \frac{\pi}{n} + \epsilon_j \right) \cos 2(t-s)k \frac{\pi}{n} \right] \quad (19)$$

Summing (18) and (19), we have

$$4 \frac{\chi_j^2 \cdot \chi_k^2}{(e_j - e_k)} \left[\cos 2(t-r)k \frac{\pi}{n} \cdot \cos 2(t-s)j \frac{\pi}{n} + \cos 2(t-s)k \frac{\pi}{n} \cdot \cos 2(t-r)j \frac{\pi}{n} \right] \quad (20)$$

Expressions such as (20) account for all terms except those involving the non-degenerate molecular orbitals [$j = 0, k = (2\gamma + 1)$]. The latter terms may also be written in this form, the contributions from the sine wave functions being zero. Since the sine factors themselves vanish, their χ 's may be chosen arbitrarily and if we take them as equal to the χ 's of the non-degenerate cosine wave functions, the above summation is still possible. Equation (4) is obtained from (20) by summation.

APPENDIX 2

It is required to obtain equation (5) from equation (4). First consider the case when j and k are conjugate molecular orbitals; putting $k = [(2\gamma + 1) - j]$ and $e_k = -e_j$ in (20) and expanding, we have

$$\frac{2\chi_j^2}{e_j} \left[\cos 2(t-s)j \frac{\pi}{n} \cdot \cos 2(t-r)j \frac{\pi}{n} \right] \left[\cos(t-r)\pi + \cos(t-s)\pi \right] \quad . \quad . \quad (21)$$

which, after the summation, is the first part of eqn. (5).

The remaining terms in $\pi_{t,rs}$ arise from the non-conjugate pairs of orbitals. Let the bonding pair conjugate with k be h ($h \neq j$). Then $k = \{(2\gamma + 1) - h\}$ and $e_k = -e_h$ and (20) becomes

$$4 \frac{\chi_j^2 \chi_h^2}{(e_j + e_h)} \left[\cos(t-r)\pi \cdot \cos 2(t-r)h \frac{\pi}{n} \cdot \cos 2(t-s)j \frac{\pi}{n} + \right. \\ \left. \cos(t-s)\pi \cdot \cos 2(t-s)h \frac{\pi}{n} \cdot \cos 2(t-r)j \frac{\pi}{n} \right] \quad . \quad . \quad (22)$$

and there is another term from the antibonding orbitals conjugate with j and the bonding orbitals h . On replacement of j by h and k by $\{(2\gamma + 1) - j\}$ equation (20) becomes

$$4 \frac{\chi_j^2 \chi_h^2}{(e_j + e_h)} \left[\cos(t-r)\pi \cdot \cos 2(t-r)j \frac{\pi}{n} \cdot \cos 2(t-s)h \frac{\pi}{n} + \right. \\ \left. \cos(t-s)\pi \cdot \cos 2(t-s)j \frac{\pi}{n} \cdot \cos 2(t-r)h \frac{\pi}{n} \right] \quad . \quad . \quad (23)$$

Summing (22) and (23), we find

$$4 \frac{\chi_j^2 \chi_h^2}{(e_j + e_h)} \left[\cos(t-r)\pi + \cos(t-s)\pi \right] \left[\cos 2(t-r)h \frac{\pi}{n} \cos 2(t-s)j \frac{\pi}{n} + \cos 2(t-r)j \frac{\pi}{n} \cdot \cos 2(t-s)h \frac{\pi}{n} \right] \quad . \quad . \quad (24)$$

which, after the appropriate double summation, is the second part of eqn. (5).

APPENDIX 3

It is required to obtain equation (14) from equation (13). Of the various terms arising in $\pi_{i,ss'}$, all except those involving the non-bonding molecular orbitals are analogous to those for the $(4\gamma + 2)$ hydrocarbons and are easily shown to be

$$2 \left[\left\{ \cos(t-r)\pi + \cos(t-s)\pi \right\} \left\{ \sum_{j=0}^{\gamma-1} \frac{\chi_j^4}{e_j} \cos 2(t-s)j \frac{\pi}{n} \cdot \cos 2(t-r)j \frac{\pi}{n} + \sum_{s=0}^{\gamma-2} \sum_{h=j+1}^{\gamma-1} 2 \frac{\chi_j^2 \chi_h^2}{(e_j + e_h)} \cos 2(t-r)j \frac{\pi}{n} \cdot \cos 2(t-s)h \frac{\pi}{n} + \cos 2(t-s)j \frac{\pi}{n} \cdot \cos 2(t-r)h \frac{\pi}{n} \right\} \right] \quad . \quad . \quad (25)$$

To this must be added the terms involving the non-bonding molecular orbitals. Suppose the non-bonding molecular orbital having a cosine wave function to be doubly occupied in the perturbed state. Then there will be one term from the j th bonding molecular orbital with a cosine wave function $[\psi_j(\cos)]$ and the sine wave function non-bonding molecular orbital $[\psi_\nu(\sin)]$ which is

$$4 \frac{\chi_j^2 \chi_\nu^2}{e_j} \left[\cos \left(2tj \frac{\pi}{n} + \epsilon_j \right) \sin \left(t \frac{\pi}{2} + \epsilon^\circ \right) \right] \left[\cos \left(2sj \frac{\pi}{n} + \epsilon_j \right) \sin \left(r \frac{\pi}{2} + \epsilon^\circ \right) + \cos \left(2rj \frac{\pi}{n} + \epsilon_j \right) \sin \left(s \frac{\pi}{2} + \epsilon^\circ \right) \right] \quad . \quad . \quad (26)$$

and there will be another term from the j th bonding molecular orbital with a sine wave function $[\psi_j(\sin)]$ and the sine wave function non-bonding molecular orbital $[\psi_\nu(\sin)]$ of

$$4 \frac{\chi_j^2 \chi_\nu^2}{e_j} \left[\sin \left(2tj \frac{\pi}{n} + \epsilon_j \right) \sin \left(t \frac{\pi}{2} + \epsilon^\circ \right) \right] \left[\sin \left(2sj \frac{\pi}{n} + \epsilon_j \right) \sin \left(r \frac{\pi}{2} + \epsilon^\circ \right) + \sin \left(2rj \frac{\pi}{n} + \epsilon_j \right) \cdot \sin \left(s \frac{\pi}{2} + \epsilon^\circ \right) \right] \quad . \quad . \quad (27)$$

Summing (26) and (27), we have

$$4 \frac{\chi_j^2 \chi_\nu^2}{e_j} \sin \left(t \frac{\pi}{2} + \epsilon^\circ \right) \left[\sin \left(r \frac{\pi}{2} + \epsilon^\circ \right) \cdot \cos 2(t-s)j \frac{\pi}{n} + \sin \left(s \frac{\pi}{2} + \epsilon^\circ \right) \cdot \cos 2(t-r)j \frac{\pi}{n} \right] \quad . \quad . \quad (28)$$

The other type of non-bonding molecular-orbital term in $\pi_{rs'}$ is from the doubly occupied, cosine wave function non-bonding molecular orbital with the antibonding orbitals. Suppose the k th pair of antibonding orbitals to be conjugate with the j th bonding pair. Then on replacement j by γ and k by $(2\gamma - j)$, the expression analogous to (28) is:

$$4 \frac{\chi_j^2 \chi_\gamma^2}{e_j} \cos \left(t \frac{\pi}{2} + \epsilon^\circ \right) \left[\cos(t-r)\pi \cdot \cos \left(s \frac{\pi}{2} + \epsilon^\circ \right) \cdot \cos 2(t-r)j \frac{\pi}{n} + \cos(t-s)\pi \cdot \cos \left(r \frac{\pi}{2} + \epsilon^\circ \right) \cdot \cos 2(t-s)j \frac{\pi}{n} \right] \quad . \quad . \quad (29)$$

Combining (28) and (29) and summing the result, we have

$$\begin{aligned}
 & 4 \left[\sin \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(s \frac{\pi}{2} + \varepsilon^\circ \right) + \cos \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(s \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos (t - r)\pi \right] \times \\
 & \qquad \qquad \qquad \left[\sum_{j=0}^{\gamma-1} \left(\frac{\chi_j^2 \cdot \chi_{\gamma-j}^2}{e_j} \right) \cos 2(t - r)j \frac{\pi}{n} \right] \\
 & + 4 \left[\sin \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(r \frac{\pi}{2} + \varepsilon^\circ \right) + \cos \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(r \frac{\pi}{2} + \varepsilon^\circ \right) \cos (t - s)\pi \right] \times \\
 & \qquad \qquad \qquad \left[\sum_{j=0}^{\gamma-1} \left(\frac{\chi_j^2 \chi_{\gamma-j}^2}{e_j} \right) \cos 2(t - s)j \frac{\pi}{n} \right] \quad . \quad . \quad (30)
 \end{aligned}$$

Combining (25) and (30) we have equation (14).

If the sine wave function non-bonding molecular-orbital is doubly occupied, the expression analogous to (30) is

$$\begin{aligned}
 & 4 \left[\cos \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(r \frac{\pi}{2} + \varepsilon^\circ \right) + \sin \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(r \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos (t - s)\pi \right] \times \\
 & \qquad \qquad \qquad \left[\sum_{j=0}^{\gamma-1} \left(\frac{\chi_j^2 \chi_{\gamma-j}^2}{e_j} \right) \cos 2(t - s)j \frac{\pi}{n} \right] \\
 & + 4 \left[\cos \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos \left(s \frac{\pi}{2} + \varepsilon^\circ \right) + \sin \left(t \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \sin \left(s \frac{\pi}{2} + \varepsilon^\circ \right) \cdot \cos (t - r)\pi \right] \times \\
 & \qquad \qquad \qquad \left[\sum_{j=0}^{\gamma-1} \left(\frac{\chi_j^2 \chi_{\gamma-j}^2}{e_j} \right) \cos 2(t - r)j \frac{\pi}{n} \right] \quad . \quad . \quad (31)
 \end{aligned}$$

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