Interaction Independent π Bond Orders
for Certain Excited States

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Particular solutions of the π bond order equations are shown for certain excited states, common to different conjugated systems and interaction-independent. The P matrix for these states has: 1 in the principal diagonal (charges), ± 1 in the secondary one, zero otherwise.

We shall show that particular solutions of the π bond order equations of certain excited states are common to different conjugated systems and independent of the details of interactions. They only depend on the molecule's symmetry. Specifically, the solutions we are going to find correspond to molecules having a twofold symmetry axis not passing through any of the $N\pi$-electron centers. The labelling is such that the symmetry establishes an equivalence between the μ and the $N + 1 - \mu$ atomic orbitals.

The mobile LCAO bond order is defined [1] as the symmetric part of

$$P_{\mu\nu} = \sum_i x_{i\mu} n_i y_{i\nu}; \quad y_{i\nu} = \sum_\varrho S_{\nu\varrho} x_{i\varrho} \tag{1}$$

where $x_{i\mu}$ is the coefficient of atom μ in the i-th molecular orbital (MO); n_i is the i-th occupation number and $S_{\nu\varrho}$ is the overlap between the atomic orbitals ν and ϱ.

We have

$$\text{Tr } \boldsymbol{P} = \sum_i n_i = N = \text{total number of } \pi \text{ electrons.} \tag{2}$$

It is easily seen (due to the orthogonality relations) that

$$P_{\mu\nu}^2 = \sum_\varrho P_{\mu\varrho} P_{\varrho\nu} = \sum_i x_{i\mu} n_i^2 y_{i\nu} \tag{3}$$

so that, if a matrix $\boldsymbol{Q}$ is defined by

$$\boldsymbol{Q} = \boldsymbol{P} - \boldsymbol{I}; \boldsymbol{I} \text{ being the unit matrix} \tag{4}$$

$$Q_{\mu\nu}^2 = \sum_i x_{i\mu} (n_i - 1)^2 y_{i\nu}. \quad \text{Similarly} \quad Q_{\mu\nu}^3 = \sum_i x_{i\mu} (n_i - 1)^3 y_{i\nu}. \tag{5}$$

Now, as $(n_i - 1)$ is ± 1 or 0, $(n_i - 1)^3 = n_i - 1$; therefore

$$\boldsymbol{Q}^3 = \boldsymbol{Q}. \tag{6}$$

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From (4) we have for neutral molecules (Tr $P = N$)

$$\text{Tr } Q = 0 . \tag{7}$$

From the eigenvalue equation

$$\sum_{\nu} H_{\mu\nu} x_{i\nu} = y_{i\mu} E_i \tag{8}$$

we deduce

$$\sum_{\nu} H_{\mu\nu} P_{\nu\varrho} = \sum_{i} y_{i\mu} E_i n_i y_{i\varrho} \tag{9}$$

which imply the equation HP = symmetric, or equivalently, due to the symmetry of the Hamiltonian

$$HQ = \text{symmetric.} \tag{10}$$

Eqs. (6), (7), and (10) will be our basic equations.

Two non-trivial solutions for Q, bearing in mind that

$$H_{\mu, N+1-\nu} = H_{\nu, N+1-\mu} \tag{11}$$

are

$$Q_{\mu\nu} = \pm \delta_{\mu, N+1-\nu}; \quad \text{i.e. } Q = \pm \begin{pmatrix} 0 & & 1 \\ & \diagdown\diagup & \\ 1 & & 0 \end{pmatrix} \tag{12}$$

which satisfies Eq. (10) and also (7) as, N being even, $\delta_{\nu, N+1-\nu} = 0$.

Besides, $Q^2 = 1$ (cf. (6)).

The corresponding P's are

$$P^{\pm}_{\mu\nu} = \delta_{\mu\nu} \pm \delta_{\mu, N+1-\nu} \quad \text{i.e. } P^{\pm} = \begin{pmatrix} 1 & & \pm 1 \\ & \diagdown\diagup & \\ \pm 1 & & 1 \end{pmatrix} . \tag{13}$$

Note that $P^+ P^- = O \quad P^+ + P^- = 2I$.

As these P are symmetric, they are identical to the total π bond order matrix. The particular solutions (13) imply unitary charges.

The occupation numbers corresponding to (13) can be obtained in the following way:

Taking the $+$ sign

$$P^+_{\mu\nu} = \delta_{\mu\nu} + \delta_{\mu, N+1-\nu} = \sum_{i} n_i (x^+_{i\mu} y^+_{i\nu} + x^+_{i\nu} y^+_{i\mu}) . \tag{14}$$

Multiplying by $x^+_{j\mu}$ and using $\sum_{\mu} x_{i\mu} y_{j\mu} = \delta_{ij}$ we obtain

$$x^+_{j\mu} = x^+_{j, N+1-\mu} = x^+_{j\mu} n_j . \tag{15}$$

If $x_{j\mu}$ correspond to a symmetric wave function, then $x_{j, N+1-\mu} = x_{j\mu}$. Therefore

$$n_j = 2 \quad \text{(if } j \text{ labels a symmetric MO)} \tag{16}$$

and

$$n_j = 0 \quad \text{(if } j \text{ labels an antisymmetric MO).} \tag{17}$$

For

$$P_{\mu\nu}^- = \delta_{\mu\nu} - \delta_{\mu, N+1-\nu} \tag{18}$$

we obtain similarly

$$\begin{aligned} n_j &= 2 \quad \text{(for antisymmetric MO's)} \\ n_j &= 0 \quad \text{(for symmetric MO's).} \end{aligned} \tag{19}$$

Now we can state the following rule:

In any conjugated system with even number of π electrons and centers, possessing a twofold symmetry axis which does not contain π centers, the bond order matrix of the state which has all symmetric (antisymmetric) energy levels doubly occupied has unitary π charges and mobile bond orders zero except those of the secondary diagonal, corresponding to symmetrically equivalent centers, which are equal to 1 (−1).

It should be stressed that this rule is independent of any specific form of the Hamiltonian as long as it has the assumed symmetry (Eq. 11).

When $S = I$, there exists a very simple relation for the energy difference between the two above mentioned states.

If electron interaction is not taken explicitly into account, $H = H^0$ we have

$$\text{Tr}\,(H^0 P) = \sum_i n_i E_i = E_\pi, \tag{20}$$

$$\sum_{\mu\varrho} H_{\mu\varrho}^0 P_{\varrho\mu}^\pm = \sum_\mu (H_{\mu\mu}^0 \pm H_{\mu, N+1-\mu}^0). \tag{21}$$

Therefore:

$$E_\pi^+ - E_\pi^- = 2 \sum_\mu H_{\mu, N+1-\mu}^0 = 4(H_{1N}^0 + H_{2N-1}^0 + \dots H_{\frac{1}{2}N, \frac{1}{2}N+1}^0) \tag{22}$$

which, in Hückel's approximation, reduces to

$$E_\pi^+ - E_\pi^- = 4m\beta \tag{23}$$

where β has the usual meaning and m is the number of pairs of equivalent centers which are first neighbours. For a linear system (chain) $m = 1$ and for a cyclic molecule, m is the number of bonds transverse to the twofold symmetry axis (see Fig. 1). That is, $E_\pi^+ - E_\pi^-$ is greater for cyclic molecules than for chains and proportional to m in Hückel's approximation.

Allowing for electron interaction in a way, for instance, similar to Hall's [2] (which is a generalization of Pople's [3])

$$H_{\mu\nu} = H_{\mu\nu}^0 + c_{\mu\nu} P_{\mu\nu}^\pm = H_{\mu\nu}^0 + c_{\mu\mu}\delta_{\mu\nu} \pm c_{\mu, N+1-\mu}\delta_{\mu, N+1-\nu} \tag{24}$$
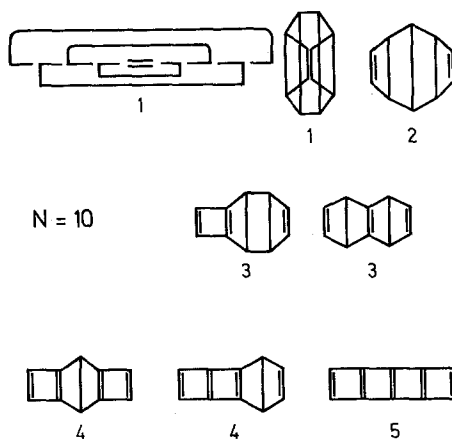
where $c_{\mu\nu}$ are appropriate parameters.

Fig. 1. A sequence of molecules indicating the common solutions for $P^{\pm}$. Under each molecule m, the number of effective bonds crossing the twofold symmetry axis, has been indicated

The total π energy is now [4]:

$$E_{\pi}^{\pm} = \tfrac{1}{2}\mathrm{Tr}(\boldsymbol{H}\boldsymbol{P}^{\pm}) + \tfrac{1}{2}\mathrm{Tr}(\boldsymbol{H}^{0}\boldsymbol{P}^{\pm}) = \tfrac{1}{2}\sum_{\mu}(2H_{\mu\mu}^{0} + c_{\mu\mu} + c_{\mu,N+1-\mu} \pm 2H_{\mu,N+1-\mu}^{0}). \quad (25)$$

Then

$$E_{\pi}^{+} - E_{\pi}^{-} = 2\sum_{\mu} H_{\mu,N+1-\mu}^{0}. \quad (26)$$

Therefore, the electronic correlation introduced does not modify the difference in energy given by (22).

In chains of even alternant systems, the state which has all symmetric energy levels doubly occupied has $N/2$ bond orders equal to one, of which only the middle bond involves neighbouring atoms. The others would correspond to different ways of "closing" the chain. This applies to molecules such as chains of AH, azapolyenes, borazapolyenes, etc., provided always the existence of a twofold symmetry axis as required. We had met this kind of solutions for butadiene using $\boldsymbol{H}^{0}$ and $\boldsymbol{H}$ of the type (24) [5], and we have shown that their existence is quite independent from any approximation used.

Let us remark a peculiar feature of the solutions we have found, namely that any molecule of the assumed symmetry shall have unitary charges in the two mentioned states, regardless of the nature of its atoms. It is as if in these states the electronegative differences cancelled out.

As an illustration, the figure shows a possible sequence of molecules which, for a given N, share the common solutions for $P^{\pm}$. Under each molecule, m is indicated, the sequence being thus in increasing order of $E_{\pi}^{+} - E_{\pi}^{-}$.

Finally, it should be pointed out that if there are more than one (non-equivalent) twofold symmetry axis in the molecule, then more particular solutions of the type described must exist.

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