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Topological Constraints on HMO Hetereoatom Parameters

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Within the Hückel molecular orbital framework, the effect of topological factors on the selection of heteroatom parameters for heteroconjugated systems is discussed.

Introduction

Although a large number of advanced computational techniques[1] (ab initio or semiempirical[2-4] eg. AM1 and PM3) are available for the quantum chemical investigation of molecules, the simple Hückel molecular orbital (HMO) approach continues to be in prevalent use because of its clear connection with molecular topology, which enables one to envisage directly how topological changes affect eigenvalues and eigenvectors. For many years, the HMO approach has been applied exclusively to polyene systems and, with certain modifications, to heteroconjugate systems.

Heteroatoms may be approached in the HMO method by appropriate changes in the empirical α and β parameters associated with each atom and bond[5]. The problem arises of the specific values to be used for various heteroatoms. The ideal procedure for evaluating heteroatom parameters would start with a correlation between some experimental property and a calculated quantity established for a hydrocarbon system and would follow with an application of this correlation to a number of compounds containing one or more of the heteroatoms under examination with a systematic variation[5]. Unfortunately, more often, parameter values have been assigned as guesses partly based either on theory or on applications of assumed validity. The result has been a profusion of parameter values in the literature[5-8]. In all the guesses for heteroatom parameters, the effective nuclear charge of the atoms have played an important role, but the topology of the system has been overlooked so far. Below, some light has been put on the topological constraints involved in the choice of these parameters.

Theory

Assume that graps $G(2n, e)$ and $G'(2n, e)$ stand for two even alternant systems possessing $2n$ vertices and e edges (chemically speaking, the number of atoms ($2n$) and bonds (e) involved in conjugation). Furthermore, let them be isoconjugate systems such that the corresponding chemical system for G' can be obtained theoretically from the chemical form of G by means of a certain set of centric perturbations[9].

Suppose the molecular orbital energies ε_j for molecular orbital ψ_j and the coefficients c_{ju} of the atomic orbital ϕ_u have a relationship that may be expressed as follows:

$$\phi_j = \sum_{u=1}^{2n} c_{ju}\phi_u \tag{1}$$

and ε_j is calculated according to

$$\varepsilon_j = < \psi_j|H|\phi_j > \tag{2}$$

where H is Hamiltonian operator. Then the effect of any perturbations involving center p and bond pr on the j_{th} molecular energy is given by

$$\delta\varepsilon_j = \sum_p c_{jp}^2 \delta\alpha_p + 2\sum_{(p-r)} c_{jp}c_{jr}\delta\beta_{pr} \tag{3}$$

where the symbol $(p-r)$ indicates that the summation extends only over the perturbed bonds between those centers that are linked together in the σ-skeleton. The symbols α and β stand for Coulomb and resonance integrals, respectively. Inserting $\delta\alpha_p = h_p\beta$ and $\delta\beta_{pr} = k_{pr}\beta$, eq. 3 becomes

$$\delta\varepsilon_j = \sum_p h_p c_{jp}^2 \beta + 2\sum_{(p-r)} c_{jp}c_{jr}k_{pr}\beta \tag{4}$$

where h_p and k_{pr} are known as heteroatom parameters. With the substitution of $\delta\varepsilon_j = X_j' - X_j$, eq. 4 can be rearranged to (in β units).

$$X_j' = X_j + \sum_p h_p c_{jp}^2 + 2\sum_{(p-r)} c_{jp}c_{jr}k_{pr} \tag{5}$$

where X_j' and X_j stand for j^{th} molecular orbital energies of the perturbed and unperturbed systems (in β units), respectively.

Now, let E_n be an n-dimensional Euclidean linear space[10,11] and vectors A and B defined as

$$A(X_1', X_2', ..., X_n') \quad B(1, 1, ..., 1)$$

Then the following equations are true for the scalar product[11,12] of these vectors.

$$(A, B) = \sum_{i=1}^{n} X_i' \tag{6}$$

$$(A, B) = (n\sum_{i=1}^{n}(X_i')^2)^{1/2}\cos Q \tag{7}$$

where Q is the angle between these vectors. Combining eqs. 6 and 7, then solving for cos Q, one obtains

$$\cos Q = \sum_{i=1}^{n} X_i'/(n\sum_{i=1}^{n}(X_i')^2)^{1/2} \tag{8}$$

Let

$$g = \sum_{i=1}^{n} X_i'/(\sum_{i=1}^{n}(X_i')^2)^{1/2} \tag{9}$$

then eq. 8 becomes

$$\cos Q = g(1/n)^{1/2} \tag{10}$$

Note that

$$\begin{aligned} &\lim \cos Q = E/2(ne)^{1/2} \\ &h_p \to 0 \\ &k_{pr} \to 0 \end{aligned} \tag{11}$$

where E and Q are the total π-electron energy and the angle of total π-electron energy of the unperturbed system, respectively.

Upper and Lower Bounds for g.

Since $\cos Q =< 1$, eq.10 yields $g =< n^{1/2}$. On the other hand, eq. 9 can be converted into

$$g^2 = 1 + 2\sum_{i<j}^{n} X_i' X_j' / \sum_{i=1}^{n} (X_i')^2 \tag{12}$$

Since X_i and X_j stand for occupied molecular orbital energies that are all positive in sign then eq. 12 yields $g >= 1$. Hence,

$$1 =< g =< n^{1/2} \tag{13}$$

Results and Discussion

Since g is an implicit function of h_p and k_{pr} (see eqs. 5 and 9), ineq. 13 clearly indicates the importance of topological factors on the selection of heteroatom parameters h_p and k_{pr}. Another important implication of ineq. 13 is that h_p and k_{pr} should not be chosen independently from each other. Especially for small systems, g is confined to a narrow range. The interpretation of ineq. 13 in chemical terms is that for a heteroatom taking part in conjugated systems and specified by a certain hybridization type etc., there should not be any strict requirement that it be represented by the same set of heteroatom parameters (eg. nitrogen atom in pyridine and quinoline). Normally, in the literature, the adverse has been followed so far, because of the complete unawareness of the topological effects which consequently sometimes causes poor correlation between the observables of the system being studied and HMO results. Fortunately, for large systems possessing high values of n, the range of freedom to choose a set of heteroatom parameters is much greater, so that the neglect of topological implements is justifiable. However, for heteroatoms for which h_p values are assumed to be negative[8], eg. boron, silicon and germanium, etc. (more electropositive elements than carbon), one has to be more cautious and should check whether ineq. 13 is fulfilled by the preferred heteroatom parameters for the reliability and selfconsistency of he results.

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