Estimation of the HOMO-LUMO Separation

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Bounds and approximate topological formulas are derived for the HOMO-LUMO separation of alternant and non-alternant conjugated hydrocarbons and heteroconjugated systems.

INTRODUCTION

In the quantum theory of the electronic structure of molecules, the difference between the energy of the highest occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO) the so-called »HOMO-LUMO separation« plays an important role[1]. We shall denote this quantity by S.

Relatively little has been done in elucidating the relationship between molecular structure (i. e. molecular topology[2,3]) and the HOMO-LUMO separation.

Thus, in spite of several attempts in the past[4-6], the structural factors which influence S are not yet clear.

In the present work we would like to report a number of new results on S.

First we consider alternant conjugated hydrocarbons and analyse their HOMO-LUMO separation as calculated within the framework of the Hückel molecular orbital method. Non-alternant hydrocarbons and heteroconjugated systems are treated in the Appendix.

The molecular graph G will be associated with a conjugated π-electron system in the usual manner[3]. For details on graph theory and its applications in the quantum chemistry of conjugated compounds the reader is referred to the books[2,3].

Let G be the molecular graph of an alternant hydrocarbon with $2n$ carbon atoms. Let the characteristic polynomial of G be written in the form

$$P(G, x) = (-1)^n [a_0 - a_1 x^2 + a_2 x^4 - \ldots + (-1)^n a_n x^{2n}] \tag{1}$$

Let $x_1 \geq x_2 \geq \ldots x_n \geq x_{n+1} \geq \ldots \geq x_{2n}$ be the zeros of $P(G, x)$. From (1) is evident that $x_j = -x_{2n-j+1}$ for $j = 1, 2, \ldots n$. This implies $x_n \geq 0 \geq x_{n+1} = -x_n$.

Then the HOMO-LUMO separation, S, may be seen to equal $2x_n$, where of course β units have been used.

Only the case of non-zero HOMO-LUMO separation will be considered here. This occurs when x_n is positive, i. e. when $a_0 \neq 0$. Therefore it will be assumed that $x_n > 0$ and $a_0 \neq 0$.

Numerous relations for the coefficients a_j of the characteristic polynomial (1) have been obtained by use of the graph theory. We list here those relations which will be necessary for later considerations.

$$a_j \geq 0 \text{ for all } j. \tag{2}$$

Moreover, if $a_0 > 0$, then all coefficients a_j are different from zero.

$$a_o = (ASC\,(G))^2, \tag{3}$$

where $ASC(G)$ is the algebraic structure count[7] of the molecular graph G, and[8]

$$a_1 = \sum_{r,s} (ASC\,(G - r - s))^2 \tag{4}$$

where the subgraph $C - r - s$ is obtained by deletion of the vertices r and s from G. The above summation goes over all pairs of vertices contained in G.

If A is the adjacency matrix of the molecular graph G, then[9]

$$(A^{-1})_{rs} = \pm\, ASC\,(G - r - s)/ASC\,(G). \tag{5}$$

The sign of the matrix element $(A^{-1})_{rs}$ is a complicated function of the molecular topology, but will be of no relevance here.

Finally, as a straightforward consequence of the Viète formulas we have:

$$\frac{a_1}{a_o} = \sum_{j=1}^{n} \frac{1}{x_j^2}. \tag{6}$$

BOUNDS FOR HOMO-LUMO SEPARATION

Since $x_1 \geq x_2 \geq \ldots \geq x_n > 0$, we conclude that $1/x_n \geq 1/x_j$ for $j = 1, 2, \ldots, n$. Therefore,

$$\frac{1}{x_n^2} \leq \sum_{j=1}^{n} \frac{1}{x_j^2} \leq \frac{n}{x_n^2}.$$

Combining these inequalities with eg. (6), one obtains

$$2\,\sqrt{a_o/a_1} \leq S \leq 2\,\sqrt{n\,a_o/a_1}.$$

The important topological function $\sqrt{a_o/a_1}$ will be denoted by H. Hence the HOMO-LUMO separation of an alternant hydrocarbon is bounded as follows,

$$2H \leq S \leq 2H\,\sqrt{n}. \tag{7}$$

The above bounds are not narrow enough. For instance for naphthalene they give $0.915 < S < 2.046$, while the correct S value is 1.236. Nevertheless, the fact that both the upper and the lower bound in (7) are proportional to H may suggest that S too could be proportional to H also.

Now we show that three different arguments give the same first order approximate topological formula for HOMO-LUMO separation, namely

$$S \doteq S_1 = 2H. \tag{8}$$

First method. We start from the identity:

$$P\,(G, x_n) = (-1)^n\,[a_o - a_1\,x_n^2 + a_2\,x_n^4 - \ldots + (-1)^n\,a_n\,x_n^{2n}] = 0. \tag{9}$$

Since in all chemically interesting[10] examples $x_n < 1$, one can neglect x_n^4 and the higher powers of x_n in eg. (9), thus giving

$$(-1)^n [a_0 - a_1 x_n^2] \doteq 0$$

i. e.

$$x_n \doteq \sqrt{a_0/a_1} = H.$$

Second method. x_n is the smallest among the numbers x_j ($j = 1, 2 \ldots, n$). Therefore we have $1/x_n > 1/x_j$ for $j = 1, 2, \ldots, n-1$. If one neglects the terms $1/x_j^2$ ($j = 1, 2, \ldots n-1$) in the summation (6), formula (8) is obtained again.

Third method. Let k be an even integer. Then

$$\operatorname{Tr} A^{-k} = \sum_{j=1}^{2n} x_j^{-k} = 2 \sum_{j=1}^{n} x_j^{-k}.$$

From the fact that $x_n^{-k} = \max \{x_j^{-k} \mid j = 1, 2, \ldots, n\}$ we derive

$$\lim_{k \to \infty} \sqrt[k]{\operatorname{Tr} A^{-k}} = \frac{1}{x_n}$$

that is

$$S = 2 [\lim_{k \to \infty} \sqrt[k]{\operatorname{Tr} A^{-k}}]^{-1}.$$

The first approximation for S is gained by setting $k = 2$

$$S_1 = 2/\sqrt{\operatorname{Tr} A^{-2}}. \tag{10}$$

On the other hand we have

$$\operatorname{Tr} A^{-2} = \sum_r (A^{-2})_{rr} = \sum_{r,s} (A^{-1})_{rs}^2.$$

From eqs. (3), (4) and (5) we have further

$$\sum_{r,s} (A^{-1})_{rs}^2 = \sum_{r,s} \left[\frac{ASC(G-r-s)}{ASC(G)} \right]^2 = \frac{a_1}{a_0} = H^{-2}$$

which combined with eg. (10) yields once again eg. (8).

Due to relation (7), the first order approximate formula (8) necessarily underestimates the correct value of S. However, a second order formula for S can be derived, which is again proportional to the topological function H, namely

$$S \doteq S_2 = H \frac{3n-1}{n}. \tag{11}$$

A similar, but considerably less accurate estimate was offered in Ref. 6.

Previously we have derived the approximation $x_n \doteq H$. But H is not an exact zero of the characteristic polynomial and therefore $P(G, H) \neq 0$. The Newton method gives

$$x_n \doteq H - P(G, H)/P'(G, H)$$

i. e.

$$S \doteq S_2 = 2H - 2P(G, H)/P'(G, H). \tag{12}$$

In order to estimate satisfactorily the values of $P(G, H)$ and $P'(G, H)$, we shall use the approximation[6]

$$P(G, H) \doteq (Ux^2 - V)^n$$

which for $V^n = a_0$ and $nV^{n-1}U = a_1$ reproduces the characteristic polynomial for small values of the variable x. Now, $V = (a_0)^{1/n}$; $U = a_1(a_0)^{1/n}/(na_0)$ while $P(G,H) \doteq (-1)^n a_0 (1 - 1/n)^n$; $P'(G, H) = (-1)^{n-1} 2 \sqrt{a_0 a_1} (1 - 1/n)^{n-1}$. Substitution of these latter relations back into (12) yields eq. (11). Note that for sufficiently large n (i. e. for hydrocarbons with a sufficiently large number of atoms), formula (11) is further simplified into $S_2 = 3H$.

NUMERICAL WORK

The accuracy of the approximate formula (11) was tested on 70 hydrocarbons, namely on all alternant systems with non-zero HOMO-LUMO separation, whose MO characteristics are tabulated in Ref. 10. The least squares line

$$S = 1.1317 \, S_2 - 0.1154$$

is not very good (correlation coefficient 0.874). Much better results are obtained, however, if one considers a particular class of alternant hydrocarbons.

The following least squares correlations are calculated for (a) acyclic polyenes (6 molecules), (b) vinyl compounds (18 molecules), (c) benzenoid hydrocarbons (24 molecules), (d) polyphenyls (8 molecules) and (e) quinodimethanes (12 molecules):

$$S = 0.9421 \, S_2 - 0.0807 \qquad \text{(a)}$$
$$S = 1.1303 \, S_2 - 0.1872 \qquad \text{(b)}$$
$$S = 1.1777 \, S_2 - 0.0885 \qquad \text{(c)}$$
$$S = 0.5086 \, S_2 + 0.7484 \qquad \text{(d)}$$
$$S = 0.9868 \, S_2 - 0.1019 \qquad \text{(e)}$$

The correlation is significant in the cases (a), (b) and (e), with correlation coefficients 0.983, 0.968 and 0.976, respectively.

Satisfactory results are obtained also for benzenoid systems, where the correlation coefficient is 0.912. However, in the case fo polyphenyls there is practically no linear correlation between S and S_2 (correlation coefficient 0.613) and for this class of compounds eg. (11) cannot be used.

The main conclusion of the present work is that although the dependence between the HOMO-LUMO separation is rather complex, its gross part is reproduced by a relatively simple topological function $H = \sqrt{a_0/a_1}$. The explicit relation between H and the topology of the corresponding molecule is known and is given by eqs. (3) and (4).

APPENDIX

In the case of non-alternant hydrocarbons, the characteristic polynomial can be written as

$$P(G, x) = (-1)^n [a_0 - a_1 x^2 + a_2 x^4 - \ldots] + (-1)^n (-1)^{\frac{\gamma-1}{2}} [b_1 x - b_2 x^3 + \ldots]$$

where γ is the size of the smallest odd-membered cycle in G. In the great majority of chemically relevant cases namely when the molecule possesses n bonding, n anti-

bonding and no non-bonding MO's, all the coefficients a_0, a_1, a_2, ..., b_1, b_2, ... are positive.

Using our first method for the estimation of the HOMO-LUMO separation (neglecting x_n^3 and the higher powers), we arrive to

$$S \doteq 2 \sqrt{H^2 + g^2}$$

where

$$g = (-1)^{\frac{\gamma - 1}{2}} \frac{b_1}{2 a_1}$$

Note that $|g|$ is usually much smaller than H. The center of the HOMO-LUMO separation is calculated to be equal to g. Hence our approximation reproduces the well-known fact[4,11] that cycles of the size $4m + 1$ produce a shift of both HOMO and LUMO towards lower energies, while $(4m + 3)$ — membered cycles exhibit an opposite effect.

Let G_h be the molecular graph of a heteroconjugated (alternant) molecule with one heteroatom in the position t, and h being the weight of the loop on the vertex t.[12] Let G be the molecular graph of the pertinent parent hydrocarbon. Then the characteristic polynomial of G_h conforms to the relation

$$P(G_h, x) = P(G, x) - hP(G - t, x)$$

Let

$$P(G - t, x) = (-1)^{n-1} [c_1 x - c_2 x^3 + \ldots]$$

Then the coefficients c_1, c_2, ... are positive and

$$c_1 = \sum_r (ASC(G - r - t))^2$$

Our first method gives the following estimate for the HOMO-LUMO separation:

$$S \doteq 2 \sqrt{H^2 + f^2}$$

where

$$f = h \frac{c_1}{2 a_1}$$

The center of the HOMO-LUMO separation is equal to f, which is in good agreement with the fact that an electronegative (electropositive) heteroatom causes a shift of the orbital energy levels towards lower (higher) energies.

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SAŽETAK

Procjena HOMO-LUMO separacije

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Izvedene su ocjene i približne topološke formule za HOMO-LUMO separaciju alternantnih i nealternantnih konjugiranih ugljikovodika i heterokonjugiranih sustava.

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