

EVALUATION OF HOMO-LUMO SEPARATION AND HOMOLOGOUS LINEARITY  
OF CONJUGATED MOLECULES

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Abstract - A variational method for calculating the HOMO and LUMO energies in the framework of Huckel theory is proposed in this paper. Graphical technique is employed for the evaluation of inverse adjacency matrix and collection of Dewar numbers is selected as a trial vector. Closed formulas for a few homologous series of conjugated hydrocarbons are deduced, which offer approximate HOMO (or LUMO) values with an average deviation less than 0.003. These formulas can be used as "homologous linearity" functions for rationalizing some of physico-chemical behaviours of conjugated homologs.

INTRODUCTION

For the purpose of investigating certain observed trends restricted by chemical behaviours of molecules, a great deal of attention has been focused on the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (1). As well known, the physico-chemical qualities of conjugated systems in a homologous series show "homologous linearity", which can be well-described by defining a function in terms of the serial number of the homologs concerned (2, 3). Obviously, this function is closely related to HOMO-LUMO separations. Therefore, it seems worthwhile to develop a method which would enable one to calculate HOMO and LUMO energies in terms of simple molecular indices with respect to the homologs considered without solving the secular equation of Huckel matrix.

Based on previous work by G.G.Hall (4) and a Yugoslavian group (5-7), a variational procedure starting from the evaluation of inverse matrix is outlined in this paper. The absolute value of HOMO or LUMO energy is calculated via

$$x_{\min} = \pm \left( \frac{CC!}{CBB'C'} \right)^{\frac{1}{2}} \quad (1)$$

where  $B = A^{-1}$  representing the inverse of adjacency matrix, C denotes a trial vector expressed in a row, B' and C' are transpose of B and C respectively. The entries of B can easily be worked out by means of graphical technique (8, 9), particularly in cases of alternants, of which the absolute values are equal to Pauling bond orders (10). The trial vector C is selected as collection of Dewar numbers (11), which can be obtained readily from the diagonal set of entries of BB'. Thus, Eq.(1) can be conveniently used for both

individual molecule and homologs. In the latter case, the "homologous linearity" will be better understood. Moreover, the significance of terminal group effect (2, 3) is turned out to be obvious.

#### EVALUATION OF INVERSE ADJACENCY MATRIX

Let the characteristic matrix  $M$  be defined as follows

$$M = xI - A$$

where  $A$  represents adjacency matrix with respect to a molecular graph  $G$ ,  $I$  stands for unit matrix and  $x$  is a variable. As is well known, the secular equation in Huckel theory can be transformed into a form identical to the determinant of  $M$ . Moreover, it is often necessary to expand the secular equation in order to obtain the characteristic polynomial for practical use, namely

$$P_G(x) = \det(M) = x^n + \dots + a_{N-1}x + a_N \quad (2)$$

where coefficients  $a_N$  and  $a_{N-1}$  play an important role, which can be easily evaluated by means of current approaches (12).

In order to obtain the entries of inverse adjacency matrix, the previous result for evaluation of  $M^{-1}$  can be conveniently reduced to the following equation by putting  $x = 0$  (12)

$$\begin{aligned} (A^{-1})_{ii} &= a_N(G-v_i)/a_N(G) \\ (A^{-1})_{ij} &= \sum_k a_N(G-(ij)_k)/a_N(G) \end{aligned} \quad (3)$$

where  $G-v_i$  arises when vertex  $v_i$  and its incident edges are deleted simultaneously from  $G$ ,  $(ij)_k$  is used to denote a path  $k$  which connects vertices  $v_i$  and  $v_j$ ,  $G-(ij)_k$  has the same meaning as  $G-v_i$ . Therefore, the inverse adjacency matrix can be evaluated in terms of  $a_N$  of molecular graph  $G$  and its sub-graphs according to Eq.(3).

The second formula available for evaluation of  $A^{-1}$  takes the following form (12)

$$(A^{-1})_{ij} = \pm [a_N(G-v_i)a_N(G-v_j) - a_N(G)a_N(G-v_i-v_j)]^{1/2} / a_N(G) \quad (4)$$

which can be simplified further in cases of even alternants as

$$a_N(G-v_i) = a_N(G-v_j) = 0 \quad (5)$$

For benzenoid hydrocarbons, the phase factor in Eq.(4) can be determined since all terms appearing have the same signs. By using Kekule structures instead of  $a_N(G)$  (13), a compact formula for evaluating entries of  $A^{-1}$  is obtained

$$(A^{-1})_{ij} = (-1)^{(n+n')/2} K(G-v_i-v_j)/K(G) \quad (6)$$

where  $n'$  represents the number of vertices of the longest path between  $v_i$  and  $v_j$ . Eq. (6) shows that the entries of inverse adjacency matrix are related to Pauling bond orders (10). Similarly, one should use  $ASC(G)$ , the algebraic count (14), instead of  $a_N(G)$  in the case of alternant containing 4m-membered rings, then

$$(A^{-1})_{ij} = \pm ASC(G-v_i-v_j)/ASC(G) \quad (7)$$

where the sign is undetermined.

The calculation can be simplified furthermore by distinguishing the vertices of alternants as star and unstar species, thus  $A$  and  $A^{-1}$  are simultaneously turned to block forms like

$$A^{-1} = \begin{pmatrix} 0 & B \\ B' & 0 \end{pmatrix} \quad (8)$$

where 0 stands for an array of zero entries. This makes the calculation decrease to one fourth of the entries.

#### SELECTION OF THE TRIAL VECTOR

Because matrices  $A$  and  $A^{-1}$  are exchangeable, they have a common eigenvector with eigenvalues reciprocal to each other, namely

$$AC = xC, \quad A^{-1}C = x^{-1}C \quad (9)$$

where  $C$  represents the eigenvector,  $x$  and  $x^{-1}$  denote eigenvalues. Eq. (9) states that the maximal eigenvalue of  $A$  corresponds to the minimal eigenvalue of  $A^{-1}$  and vice versa. Therefore, the minimal eigenvalue of  $A$  can be obtained by means of evaluating the maximal eigenvalue of  $A^{-1}$ . Obviously, variation principle is suitable for solving such a problem, which gives the upper bound of the exact value. Since the accuracy of the calculated eigenvalue is greatly dependent on the accuracy of the trial vector, in order to obtain good numerical result, one must find out a well-behaved trial vector.

According to Huckel theory, the molecular orbital coefficient of the  $i$ -th atom satisfies the following equation

$$c_i^2 = P_{G-v_i}(x) \quad (10)$$

Because the minimal eigenvalue is close to zero, therefore Eq. (10) can be approximated by two terms as

$$c_i^2 = a_N(G-v_i) + x a_{N-1}(G-v_i) \quad (11)$$

This reveals that a set of  $a_{N-1}(G-v_i)$ , namely Dewar numbers, can be reasonably selected as the trial vector

$$C = (a_{N-1}(G-v_1), a_{N-1}(G-v_2), \dots, a_{N-1}(G-v_n)) \quad (12)$$

for an even alternant. As is well known (11), Dewar number measures the position reactivity of conjugated molecule concerned, trial vector (12) is expected to be well-behaved as one of the zero-order frontier orbitals.

For more efficient calculation, square of the inverse matrix is used instead. This enables the alternants to have

$$A^{-2} = \begin{pmatrix} BB' & 0 \\ 0 & B'B \end{pmatrix} \quad (13)$$

with star and unstar components satisfying

$$(BB') C = x^{-2} C, \quad (B'B) C = x^{-2} C \quad (14)$$

By means of variation principle, Eq.(1) can be readily derived.

It can be verified by Eq.(7) that  $a_{N-1}(G-v_i)$  is proportional to the  $i$ -th diagonal entry of  $BB'$ , namely

$$(BB')_{ii} = a_{N-1}(G-v_i)/a_N(G) \quad (15)$$

Therefore, it is possible to obtain the trial vector directly from the diagonal set of  $BB'$ . Phase factors of components of the trial vector are determined by means of maximizing the denominator of Eq.(1) so that the optimized minimal eigenvalue can be obtained.

#### CLOSED FORMULAS OF HOMOLOGOUS SERIES

By means of the method presented, not only individual members but also the whole series can be treated once for all. Closed formulas of HOMO (or LUMO) energy in terms of topological parameters such as number of carbon atoms or number of repeated structure units are obtained for lots of conjugated homologous series. Here, a few typical ones are presented for illustration.

#### Polyene

Although the closed result for this series is well known, yet it seems worthwhile to calculate with the present method for illustration. Let  $n = 2m$  representing the number of carbon atoms involving in the linear chain, then one can readily write down  $B$  and  $C$  according to Eqs.(6), (12) and (15), namely

$$B = \begin{pmatrix} 1 & -1 & 1 & -1 & \dots & \pm 1 \\ 0 & 1 & -1 & 1 & \dots & \mp 1 \\ 0 & 0 & 1 & -1 & \dots & \pm 1 \\ & \dots & & \dots & & \\ 0 & 0 & 0 & 0 & & 1 \end{pmatrix}$$

$$C = (m, -(m-1), (m-2), \dots, \pm 1) \quad (16)$$

Thus, Eq.(1) leads to

$$x_{\min} = \pm \left( \frac{5}{2m^2 + 2m + 1} \right)^{\frac{1}{2}} \quad (17)$$

Both of the approximate values obtained from Eq. (17) and the corresponding accurate ones are tabulated below for comparison

Table 1. A listing of the HOMO energy levels obtained from Eq. (17) and corresponding accurate values of polyene

n	2	4	6	8	10	12	14	16
Eq. (17)	1.000	0.620	0.447	0.349	0.286	0.243	0.210	0.186
accurate	1.000	0.618	0.445	0.347	0.285	0.241	0.207	0.185

### Polyacene

Let n represent the number of six-membered rings involved in polyacene. By repeating the same procedure given above, the formula is worked out which separates into two parts with respect to  $n = 2m$  and  $n = 2m-1$ , respectively

$$x_{\min} = \pm \left[ \frac{2520(8m^2+6m+1)}{2697m^6+11088m^5+26250m^4+31815m^3+19383m^2+6237m+810} \right]^{\frac{1}{2}} \quad (n=2m) \quad (18)$$

$$x_{\min} = \pm 2 \left[ \frac{630(8m^2+1)}{2697m^6+3297m^5+11130m^4+2100m^3+3273m^2+273m+810} \right]^{\frac{1}{2}} \quad (n=2m-1)$$

In the following, numerical data obtained from Eq. (18) are again tabulated in comparison with those accurate Huckel values

Table 2. HOMO energy levels of polyacene obtained from Eq. (18)

n	1	2	3	4	5	6	7	8
Eq. (18)	1.000	0.620	0.415	0.296	0.222	0.171	0.137	0.111
accurate	1.000	0.618	0.414	0.295	0.220	0.169	0.137	0.109

### Substituted Polyene and Polyphenylene

Two examples of substituted polyene namely  $\alpha$ -mono-phenyl-polyene ( $C_6H_5(CH)_{n-1}CH_2$ ) and  $\alpha, \omega$ -diphenyl-polyene ( $C_6H_5(CH)_n C_6H_5$ ) are considered. Their HOMO energies take the following forms respectively

$$x_{\min} = \pm \left[ \frac{10(4n^3+30n^2+71n+144)}{16n^5+200n^4+1000n^3+2935n^2+5284n+5760} \right]^{\frac{1}{2}} \quad (19)$$

$$x_{\min} = \pm 4 \left[ \frac{5(32n^3+276n^2+1108n+2673)}{256n^5+4160n^4+31480n^3+134620n^2+335074n+421065} \right]^{\frac{1}{2}} \quad (20)$$

where  $n=2m$  represents the number of carbon atoms in the linear chain. Similarly, the formula of HOMO energy of polyphenylene may be derived as follows

$$x_{\min} = \pm 2^n \left[ \frac{n(26n^2-9n+1)}{3(51n^3-102n^2-3n+12)2^{2n}+(120n^2+16n-8)2^n-(36n^2+24n+4)} \right]^{\frac{1}{2}} \quad (21)$$

where n represents the number of six-membered rings involved in. Of course, one knows that there was no closed formula available for anyone of these three homologs before.

## HOMOLOGOUS LINEARITY

The variation of physico-chemical properties with respect to the number of repeated units in a homologous series has been well studied with the aid of the following equation

$$P = a + bF(n) \quad (22)$$

where  $F(n)$  is a function of  $n$  which represents the number of repeated units,  $a$  and  $b$  are constants. For the purpose of generalizing the application of Eq. (22) from polyene to substituted polyene Chiang (2) keeps  $F(n)$  invariant by shifting the argument  $n$  to  $n+t$  in order to fit the experimental results. He calls  $t$  as "terminal effect" and has tabulated the  $t$ 's for a lot of homologs. Xu and Li (3) intended to interpret it in terms of a modified model but they still kept the empirical characteristics of Chiang. Since it seems not so easy to obtain rigorous analytical  $F(n)$  other than polyene Based on the present result of this paper, it seems easier to understand the meaning of Chiang's result. Now, let  $x_{\min}$  given by Eq. (17) be taken as  $F(m)$ , then it is found that there exists some value of  $t$ , which can make the calculated data from  $F(m+t)$  almost coincide with those given by another homologs concerned. This can be well illustrated by comparing the numerical values from  $F(m+0.85)$  with those from Eq. (19) as shown below

Table 3. HOMO energy values of  $\alpha$ -phenyl-polyene obtained from Eq. (19) and from Eq. (17) by putting  $m+0.85$  instead of  $m$

$n$	2	4	6	8	10	12
$F(m+0.85)$	0.658	0.467	0.361	0.294	0.248	0.212
Eq. (19)	0.664	0.476	0.368	0.299	0.252	0.217

which states that  $\alpha$ -mono-phenyl-polyene has its terminal effect with  $t = 0.85$ . Similar result holds for other linear cases. Therefore, in Huckel sense, the "terminal effect" may be readily related to the fact that substitution at the terminal site will cause HOMO-LUMO separation for all members of the homologous series to be reduced approximately by an equal value.

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