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Eigenvalue Distributions for the Graphs of Alternant Hydrocarbons

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In order to focus attention on the eigenvalue distribution for the graphs of polyhex molecules, a hypothesis is proposed about the number of eigenvalues greater than or equal to 2. From the density of states for several polymeric series of molecules it can be deduced that this hypothesis is satisfied for many molecules but in a modified form. A more general theorem on the distribution, which can be applied to any polyhex molecule, is described briefly. The calculation of the total energies of the polymeric molecules is described, and its decomposition into the sum of terms proportional to various graphical invariants is discussed. The small but significant dependence on the number of bay regions is stressed. The term proportional to the number of Kekulé structures is also strongly reduced by an exponential of the number of rings and is related to the highest occupied orbital energy.

INTRODUCTION

The importance of the highest occupied orbital energy ϵ_{HO} (and the related lowest unoccupied orbital energy ϵ_{LU}) in determining the chemical behavior and reactivity of an alternant hydrocarbon has been accepted for some time. Along with the next highest energies, these also determine the optical spectra of the molecule. The role of the remaining orbital eigenvalues is less chemical but important to various properties of the molecule as a system.

From the earliest calculations on the Hückel theory it has been known that the entire set of eigenvalues of the Hückel matrix, when referred to an origin at α and scaled by β (which makes it the adjacency matrix A of graph theory), lie within the interval

$$3 > \epsilon > -3$$

and that, for an alternant, the eigenvalues form a mirror distribution with every positive eigenvalue ϵ matched by an-

other at $-\epsilon$. Zero eigenvalues are possible and indicate that the molecular system is a radical.

In this paper some established results on the distributions will be given, and several hypotheses will be presented which are generalizations about many known molecules. Results will be stated for the positive eigenvalues, but corresponding results are true for their mirror images. Much more work is required before the distributions are fully understood.

HYPOTHESIS ABOUT THE EIGENVALUE DISTRIBUTIONS

In an attempt to generalize about the observed distributions of eigenvalues of polyhex molecules, I set up an hypothesis. This stated that the number of eigenvalues greater than or equal to 2 should be $r/2$ for a molecule with r rings where r is even and $(r + 1)/2$ when r is an odd number. The number of eigenvalues less than 2 and greater than or equal to 1 should be $r + 1$. The remaining positive eigenvalues lie below 1.

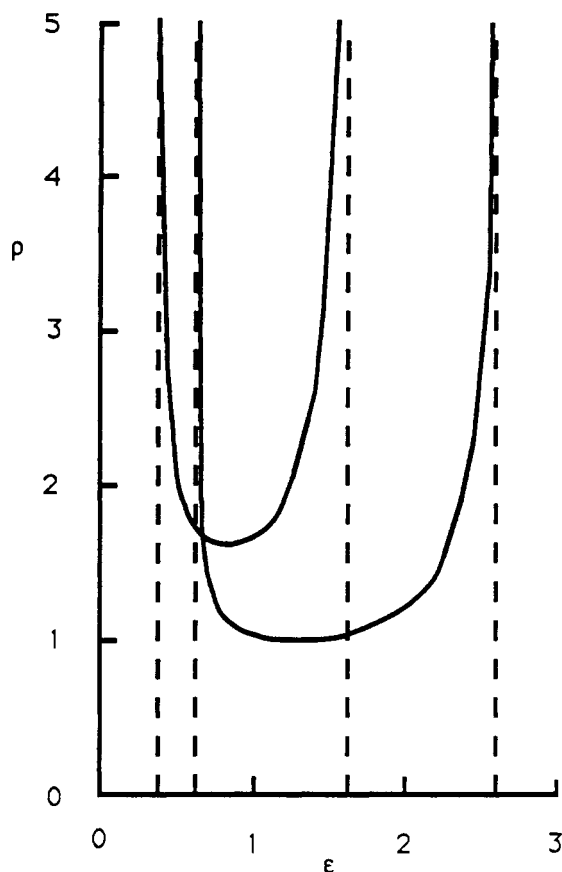


Figure 1. Density of states for the chrysene series of polymers.

These generalizations are obeyed exactly for the polyacenes. For this series the eigenvalues have been expressed in closed form¹ as

$$\epsilon = \pm 1/2[1 \pm \sqrt{(9 + 8 \cos k)}], \quad k = s\pi/(r+1), \\ s = 1, 2, \dots, (r+1)$$

except that $\epsilon = 0$ is excluded. Their distribution over the various regions can thus be verified immediately. The hypothesis is not obeyed exactly for any other series, but for many molecules, its allocations are a good approximation to the calculated distribution. Some explanations are needed!

POLYMERS AND THEIR DENSITIES OF STATES

A polymer consists of a number, n , of identical repeated units with end groups which may have a variety of structures. The eigenvalues of the graphs of such systems form a band, or bands, as the number of units increases. The band shape is independent of the nature of the end groups. Thus we can define a density of states for polymers.

Densities of states for several different polymeric series have been calculated.² A typical result is shown in Figure 1.

This is the density for the catacondensed series which consists of hexagons having bay regions along alternate sides of a central axis. The first such molecule is chrysene, so this may be called the chrysene series. It shows infinite densities at both ends of the two bands. Energies close to these will appear frequently in the eigenvalue spectra even for polymers having small n . There is a band gap between the occupied and empty bands. (The empty bands are the mirror image of the occupied bands in the $\epsilon = 0$ axis.) The polyacene series has no such band gap, and this shows the semiconductor character (and strong reactivity) of these molecules as n becomes large. The presence of a peak in the region where ϵ is greater than or equal to 2 suggests that the number of eigenvalues here may follow some rule. The evidence from the distribution is that

Table I. Number of Eigenvalues Greater than or Equal to d for Various Molecules

bual	r	R	d	no. ($\epsilon \geq d$)
	3	2	2	2
	3	2	1.83	2
	4	3	1.83	3
	6	2	2	2

there are $r/2$ [or $(r+1)/2$ for r odd] eigenvalues in the range greater than 1.902113. Thus, with a slight modification of the bound from series to series, the first part of our hypothesis is confirmed. The results for these two series reinforce the need for some more general procedure that can be applied to molecules which do not form parts of any polymeric series.

THEOREM ON THE DISTRIBUTION OF EIGENVALUES

Another approach to the problem of locating the eigenvalues without calculating them has been suggested recently by the author.³ This uses the concept of an independent red set within the molecule. From the polyhex the bual is first defined. This graph has a vertex at the center of each hexagon and an edge between two vertices whose hexagons share a common edge. A red set is a selection of these vertices no two of which are connected by an edge and whose size is as large as possible. It is not necessarily unique. The size of this set is denoted by R , the number of red hexagons. It is then shown that the number of graphical eigenvalues in the various possible regions is governed by R . The lower limit of the uppermost region, d , is given by the smallest eigenvalue of an $R \times R$ matrix, B , whose diagonal elements are all equal to 2 and which has an off-diagonal element of $1/6$ when and only when the two corresponding red hexagons have second neighbor vertices and have one CC bond connecting them. The theorem states that the number of eigenvalues greater than or equal to d is at least R .

For any catacondensed molecule the bual is a tree graph and so is bipartite. The red set is the larger of the two sets into which the vertices can be divided. The value of R for an unbranched catacondensed benzenoid is then given by $r/2$ if r is even and $(r+1)/2$ if it is odd. Branching can lead to larger values of R and three-membered rings to smaller values. For the polyacenes the theorem is easy to apply since the matrix B is diagonal and its lowest eigenvalue, and the value of d , is 2. It proves again that the number of eigenvalues greater than or equal to 2 is at least R . For the chrysene series, the results are only a little more difficult since the limit of the first region, from an estimate of the lowest eigenvalue of B , is easily shown to be $d = 1.667$. This limit is less than the exact result from the density calculations which gave $d = 1.902$, but the count of eigenvalues is increased only slightly since their density is low in this region. A selection of polyhex, as indicated by their buals, is shown in Table I together with r , R , d , and the number of eigenvalues greater than or equal to d . The red vertices are encircled.

These results illustrate the theorem above, and the identity of the final column with R means that its inequalities can here be replaced by equalities showing that the results are close to the best possible. The hypothesis that the number of the largest eigenvalues is given exactly by R is true for all these molecules.

The boundary of the next eigenvalue region is usually more difficult to calculate since a larger matrix is involved. For the polyacenes, exceptionally, it is diagonal with the smallest ei-

genvalues equal to 1. Then the extension of the theorem to the next region asserts that the number of eigenvalues greater than or equal to 1 will be at least $3R$. The exact number of these eigenvalues is $3R$ when the number of rings is odd but $3R + 1$ when it is even. For other series the boundary is smaller than 1 and less easy to calculate and so that the theorem is less useful. For most molecules the number of eigenvalues < 1 is not prescribed. The theorem thus justifies the generalizations already suggested, shows their limitations, and indicates how they have to be modified to apply to other molecules.

For molecules in general, as can be seen in Table I, the values of R are not so simply expressed in terms of r as originally suggested but vary depending on the molecular geometry. It is clear that this theorem gives good information about the higher eigenvalues and some useful information about the remaining eigenvalues.

TOTAL Π ENERGY

Using a theorem proved recently,⁴⁻⁶ it is possible to calculate the total π energy of the polymer molecules as a function of n , the number of repeating units. Asymptotically, this energy has the form

$$E_{\pi} = \alpha n + \beta + o(1)$$

where the constant α can be calculated² as an integral over the band

$$\alpha = \frac{2}{\pi} \int_0^{\pi} \epsilon(k) dk$$

with a sum of integrals when there are several bands. For some polymeric series the constant β can be calculated using the energies at the limit points of the bands. The β term is changed, but α does not, when the end groups change. The remainder term always decreases in magnitude as n increases and is usually very small compared with the first two terms, though a few exceptions have been recognized and treated.

It can be shown that the total π energy is expressible in terms of the trace of a convergent infinite power series in the matrix A . The first few terms of this series demonstrate that the two quantities, N , the number of C atoms, and M , the number of CC bonds, are the dominant quantities determining this energy. The values of α and β can both be decomposed in this way. Higher terms begin to show the need for other, more elaborate, graphical invariants. The first of these is b , the number of bay regions and another is K , the algebraic number of Kekulé structures. A study⁷ using some molecules with the same values of N , M , and K but different values of b has shown clearly the reality of the dependence on b . Empirical study of the energies of numerous molecules indicates that N , M , and b , while clearly of major importance, are not the only relevant quantities. In particular, by considering isomers, molecules with constant values of both N and M , it is clear that their energy differences correlate closely with the number of Kekulé structures. The linear relation between these

Table II. HOMO Eigenvalues of the Chrysene Series (with r Rings and K Structures) and Its Dimethylene Derivatives

r	K	$E(\text{mol})$	$E(\text{deriv})$	$E(m)/E(d)$
4	8	0.5201387	0.05703569	9.1195
5	13	0.5019240	0.03480814	14.4197
6	21	0.4714064	0.02138698	22.0417
7	34	0.4582487	0.01318402	34.7579
8	55	0.4438350	0.00814344	54.5022
9	89	0.4351486	0.00502329	86.6262

is obeyed for many series.⁸⁻¹⁰ The slope of this line varies from one isomeric series to another and decreases exponentially as the number of rings increases. The bay regions enter this calculation in a minor way and their effect can be removed to demonstrate more clearly the remaining dependence on K . Why should the energy depend on the number of Kekulé structures?

The question why such a curious term should appear in the energy deserves an answer. If the situation is examined from a different point of view, we can note that the product of the positive eigenvalues is just the value of K , the structure count. The sum of the squares of the eigenvalues is fixed by the value of M , and the sum of the fourth powers by N and M . So, for isomers, the large eigenvalues must be strictly controlled by the fixing of N and M while ϵ_{HO} , which is the one least fixed by N and M is the one most sensitive to K . This discussion has been carried further by Gutman and Hall,¹¹ who suggest that the K dependence of the energy is principally due to the term in ϵ_{HO} and that this eigenvalue is nondegenerate and proportional to K . Some empirical evidence for this can be found by comparison of the ϵ_{HO} for the chrysene series and for the derived series which has two additional bonds but the same number of rings. The latter has a fixed $K = 1$ so that the ratio of these eigenvalues should be the value of K for the former. The results are shown in Table II.

A comparison of the second and final columns of Table II shows clearly the dependence of ϵ_{HO} on K . The accuracy of the very small eigenvalues is limited by the accumulation of rounding-off errors so that the ratios are not exact.

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