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Eigenvalue distributions in alternant hydrocarbons

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A theorem due to Lord Rayleigh is applied to the graphs and bual graphs of conjugated hydrocarbon molecules to show how the distribution of their eigenvalues can be understood. A lower bound to the number of eigenvalues larger than or equal to 2 can be predicted easily from the graphs. The uses of the theorem as applied to polyenes, non-alternants and polyhex are illustrated.

1. Introduction

Information about the distribution of the orbital eigenvalues of an alternant hydrocarbon in the Hückel or graphical theory of conjugated systems has been useful in relating its chemical behaviour to its geometrical characteristics. The best-studied of these relations has been that between the frontier orbital energy and the reactivity of the molecule. It is now appropriate to consider further relations. Knowledge about the distribution generally can be used to generate approximate formulae for the total pi energy [1].

This paper demonstrates a simple method of obtaining information about the number of graphical eigenvalues greater than two and the number greater than one. Using this method, it is possible to derive such information almost from inspection of the molecular graph.

The method can be extended to give similar information about non-alternants. As a further example, the number of positive eigenvalues is discussed briefly.

2. The Rayleigh theorem

The method described here relies on a theorem due to Lord Rayleigh [2]. It can be rewritten in the present context as follows:

Given an m by m Hermitian matrix A with distinct eigenvalues ε_i, $i = 1, \dots, m$, numbered in descending order, and an arbitrary set of n orthonormal vectors v_r, $r = 1, \dots, n$, $(n < m)$ defined in the m dimensional space on which A acts, form a new Hermitian matrix E by taking all the products:

$$E_{rs} = v_r^{\mathrm{H}} A v_s, \qquad r, s = 1, \ldots, n$$

(v^{H} is the Hermitian conjugate of v.) Then let e_i be the eigenvalues of E, assuming these to be distinct and numbered in descending order. The theorem relates these to the eigenvalues of A and says that

$$\varepsilon_1 \geq e_1 \geq \varepsilon_{m-n+1}, \ \varepsilon_2 \geq e_2 \geq \varepsilon_{m-n+2}, \ldots, \varepsilon_n \geq e_n \geq \varepsilon_m.$$

Degeneracy among the eigenvalues is treated as a limiting case of this.

An immediate example of this is the well-known separation theorem. In this $n = m - 1$ and the vectors are the original basis set with one vector omitted. The inequalities then become

$$\varepsilon_1 \geq e_1 \geq \varepsilon_2 \geq e_2 \geq \varepsilon_3 \geq \ldots e_{m-1} \geq \varepsilon_m,$$

which is the usual result, showing that the original eigenvalues are separated by those of the reduced matrix. In some applications, the sum of the eigenvalues is sufficient and this is easily deduced from the trace of E.

For some purposes, a simpler form of the theorem is sufficient. In this, we label the largest and smallest eigenvalues of E as $e_>$ and $e_<$ and the theorem states that there are at least n eigenvalues of A larger than or equal to $e_<$ and at least n smaller than or equal to $e_>$. The inequalities take their simplest form when all the eigenvalues of E are equal, since then $e_< = e_>$.

These versions of the theorem allow us to embed molecular fragments within a molecule and use their eigenvalues to estimate the eigenvalues of the larger molecule. Embedding, in the strict sense, has become (see refs. [3,4]) a powerful method of identifying some special eigenvalues of molecules by embedding within them fragments whose eigenvalues are known. These fragments are surrounded by nodes and reflected fragments so that the eigenvector equations for the entire molecule are satisfied. Approximate embedding is a more flexible procedure and yields inequalities on the number of eigenvalues within certain limits rather than their exact values. If two embedded fragments do not have any common atoms, then they will be disjoint. The fragment eigenvectors, in particular, will then remain orthogonal as vectors in the space of the molecule. The operation of A on one of these eigenvectors will produce non-vanishing components at all neighbouring atoms. If any of these atoms belong to another fragment, then a non-vanishing off-diagonal element will arise in E. If each fragment is surrounded by node atoms not in any other fragment, then the off-diagonal elements of E will vanish. This greatly simplifies the application of the theorem.

In the following applications of this theorem to alternants, attention is focused on the positive eigenvalues of A. Since, for an alternant, there are as many negative eigenvalues as positive, this means that the lower inequalities are not used. For these molecules, the distribution of the negative eigenvalues mirrors that of the positive ones.

The smallest eigenvalue of a matrix can be estimated from the Levy–Hadamard theorem [5], which says that all the eigenvalues lie within the set of intervals, each of which has a diagonal element as its centre and as radius the sum of the moduli of the off-diagonal elements in the same row.

3. Application to polyenes

As a simple but useful application of the theorem, we consider the eigenvalues of polyenes which are greater than or equal to 1. For these, we use the occupied eigenvector of ethene, viz. that which has two neighbouring C atoms with coefficients of $1/\sqrt{2}$ and $\varepsilon = 1$. The ethenes are now embedded into the polyene so that there is at least one extra C atom as a node between every pair of ethenes. The number of eigenvalues greater than or equal to 1 will be at least the number of embedded ethenes. Two examples are shown in fig. 1. Butadiene has one embedded ethene and, in fact, has one eigenvalue greater than one. 3-vinyl-hexatriene has three ethenes and also has three such eigenvalues. This suggests that the theorem may give a good estimate of the exact number of these eigenvalues.

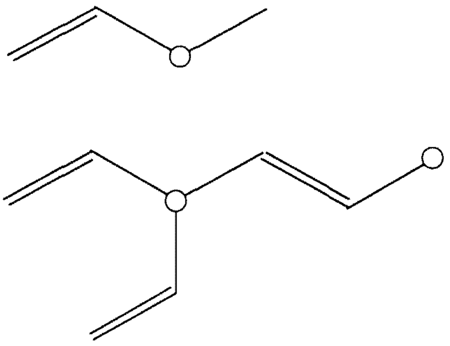

Fig. 1. Embedding ethenes in polyenes.

The ethenes are shown in fig. 1 as double bonds and the separating atoms as zeros. Since they do not overlap, the three vectors are orthogonal and, since there is a node atom between every pair, the matrix E has zero matrix elements between them. Thus, the E matrix is diagonal with unit elements on the diagonal. The number of ethenes placed in the original skeleton will then determine the minimum number of eigenvalues greater than or equal to 1. This number will be called the *white* number W of the molecule.

The white numbers for the linear polyenes are easily deduced. The atoms are divided into groups of three from one end. The first two are the ethene and the third the node. Thus, for these molecules or radicals, $W = \lfloor (n+1)/3 \rfloor$, where this symbol indicates the largest integer less than the argument. For the annulenes, the white number is $W = \lfloor n/3 \rfloor$. Since the eigenvalues of these polyenes are known, these numbers can be verified to be the correct numbers. The presence of branching complicates the evaluation of W. Some examples are shown in table 1 to illustrate the variety of results. These results show that W is more than just a lower limit, but is indeed a good estimate of $\#(e \geq 1)$, the actual number of eigenvalues greater than or equal to 1. Only the final example is different and this is the only non-polyene. The presence of a ring complicates the calculation and a separate treatment is needed.

Table 1

White and green numbers and numbers of eigenvalues.

Molecule/radical	n	W	$\#(e \geq 1)$	G	$\#(e \geq \sqrt{2})$
3-vinyl-butadiene	6	2	2	1	1
3-vinyl-hexatriene	8	3	3	1	1
2,3-divinyl-butadiene	8	2	2	1	1
trivinyl-methyl	7	3	3	1	1
benzyl	7	2	3	1	1

Another embedding which is easy to apply uses the largest eigenvalue of the radical trimethylene methyl. This has $\varepsilon = \sqrt{3}$. A polyene which has one branch point, such as 3-vinyl-hexatriene in table 1, can have one such embedding so that at least one eigenvalue will be greater than or equal to $\sqrt{3}$ and, for this example, exactly one is found. When there are several branch points, it will be necessary to fit this radical fragment into the molecule with separating C atoms as nodes in order to estimate the number of these eigenvalues.

More information is often found by applying the matrix A to each vector twice to give the squared matrix S:

$$S_{rs} = u_r^{\mathrm{H}} A^2 u_s, \quad r, s = 1, \ldots, n.$$

For alternants, including polyenes, A can be partitioned as

$$A = \begin{pmatrix} O & B \\ B^{\mathrm{T}} & O \end{pmatrix},$$

and A^2 becomes

$$A^2 = \begin{pmatrix} B^{\mathrm{H}}B & O \\ O & BB^{\mathrm{H}} \end{pmatrix},$$

but B^HB and BB^H have the same non-zero eigenvalues, so only one need be considered. Since the atoms interact only with those in the same alternant set and the vectors u_r can be divided into v_r involving only the starred atoms and w_r the unstarred, the matrix S divides into two matrices,

$$X_{rs} = w_r^H B^H B w_s, \qquad Y_{rs} = v_r^H B B^H v_s,$$

and only one of X and Y is necessary. The square-root of the lowest eigenvalue of this matrix gives a tighter lower bound for the n largest eigenvalues of the molecule. The second matrix gives the same results, and these account for the negative eigenvalues of A which have the same squares as the positive ones. This process can be put into graphical form by introducing the square graphs. These are formed by joining the atoms of A that belong to the same alternant set by edges if the atoms are second neighbours. Since the graph of A is bipartite, there are two such unconnected graphs. By adding a weight at each vertex equal to the degree of that vertex in A, the graphs become a representation of B^HB and BB^H. For benzenoids, these graphs contain triangles and so are not bipartite. X is derived from the B^HB graph using the w_s vectors, and Y from BB^H, just as E is derived from A.

An *independent* set of vertices of a graph is defined as a set no two of whose members are connected by an edge (see, for example, ref. [6]). The selection of an independent set can be regarded as the first stage in the colouring of a graph. All the members of such a set are given the same colour. A bipartite graph has two independent sets. A graph containing triangles has at least three, since the three vertices must have different colours (see appendix). For a squared graph, the largest set of independent vertices which are not of degree 1 can be calculated as its *green* number (G). It gives the lower bound to the number of eigenvalues of A which are greater than or equal to $\sqrt{2}$. Examples of G and $\#(e \geq \sqrt{2})$ are shown in table 1.

4. Eigenvectors for benzene

We begin by listing the positive eigenvalues and eigenvectors for benzene. These are shown in fig. 2:

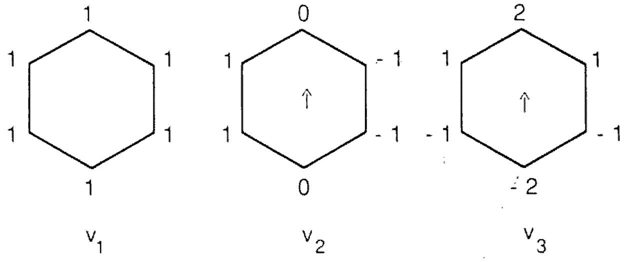

Fig. 2. Positive eigenvectors for benzene.

v_1 is then normalized by dividing each component by $\sqrt{6}$, v_2 by 2 and v_3 by $2\sqrt{3}$. The eigenvalues are 2, 1, 1, respectively. We note that the first has no preferred direction, whereas the second and third depend on the direction taken as vertical and are indicated by an arrow inside the hexagon.

It is now trivial to embed these in the benzyl radical to show that it will have at least one eigenvalue larger than or equal to two, and two more larger than or equal to one.

5. The red set of a polyhex

From the graph of any polyhex, a new graph can be constructed by placing a vertex at the centre of each hexagon and joining these with an edge when the two hexagons share a common edge. This is called the *bual* [7] of the molecule (various other names for this have been suggested). For a catacondensed polyhex, the bual is a tree and so is bipartite. Its vertices can be coloured using only two colours. For these polyhex, we define the *red set* as the coloured set with the larger number of vertices. In general, however, the bual of a polyhex is not a bipartite graph, but we can imagine the first stage in the colouring of its vertices to be the selection of an independent set with the maximum number of vertices (see appendix). This will be the *red set*. The red vertices (red hexagons in the original polyhex) have the property that no two reds are nearest neighbours. The remaining vertices may require several colours, but we do not need this information. Some molecules possess several alternative red sets which are of equal size. It is then an advantage to select one of these that has the largest $e_<$. The number of vertices in the red set will be called the red number (R) of the polyhex. For unbranched catacondensed molecules, and for all with bipartite buals, $R = \lfloor (r+1)/2 \rfloor$ when the number of rings is r.

6. The upper eigenvalues

In this application of the Rayleigh theorem, the vectors are defined as the normalized v_1 vectors (see fig. 2) for the hexagons whose vertices form the red set. The matrix E derived from this set has R rows and columns, and its matrix elements are determined as follows:

$$\begin{aligned} E_{rs} &= 2, && r = s; \\ &= 0, && \text{if } r \text{ and } s \text{ have one vertex between them in a straight line;} \\ &= 1/6, && \text{if } r \text{ and } s \text{ are joined to an intermediate vertex making a } 120^\circ \text{ angle connection;} \\ &= 0, && \text{if } r \text{ and } s \text{ are more distant.} \end{aligned}$$

The meaning of these distinctions is clarified in fig. 3. The red vertices are denoted by a circle around the vertex. Clearly E will be in diagonal form if all the red

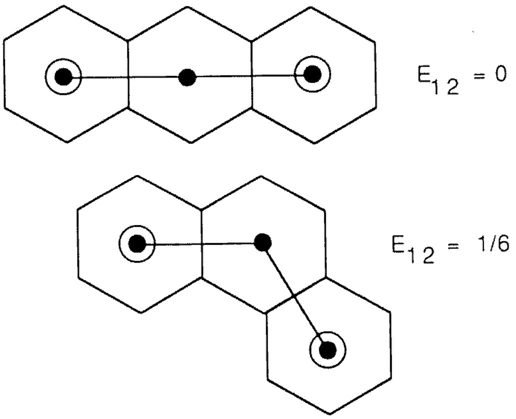

Fig. 3. Matrix elements between red vertices.

vertices are in rectilinear relations to one another. The R-fold degenerate eigenvalue is then 2. Thus, for these molecules, the theorem gives R as a lower bound to the number of eigenvalues of A which are greater than, or equal to, 2. Since the red set has been chosen to maximize the number of vectors, this is often exactly the number of these eigenvalues. (There must also be at least R eigenvalues less than 2, but this is an underestimate of their number.) If the red vertices involve angular connections, it may be better to use a smaller set of vertices which are further apart so that all the interactions vanish and E becomes diagonal. When E is not diagonal, an estimate of $e_<$, its lowest eigenvalue, is required. Since a lower limit to this is sufficient, an approximation can be found using the Levy–Hadamard theorem as above. The Rayleigh theorem then bounds the number of eigenvalues greater than or equal to $e_<$. When $e_<$ is close to 2, this bound may be very close to the actual number of eigenvalues. A better estimate of $e_<$ can sometimes be found using the squared matrix S.

7. Lower eigenvalues

The Rayleigh theorem and the red set can also be used with the eigenvectors v_2, v_3 of fig. 2, corresponding to the eigenvalue 1, or with some subset of them since all are orthogonal. This v_2 vector has a natural vertical direction corresponding to the line between the nodes. It is convenient to give all the hexagons in the set the same direction. The matrix elements of A between these v_2 vectors belonging to the red hexagons are defined as

$C_{rs} = 1$, $r = s$;

$= 0$, r and s second neighbours in the same horizontal or vertical line;

$= -1/4$, r and s with angular connection as in fig. 4;

$= 0$, if r and s more distant.

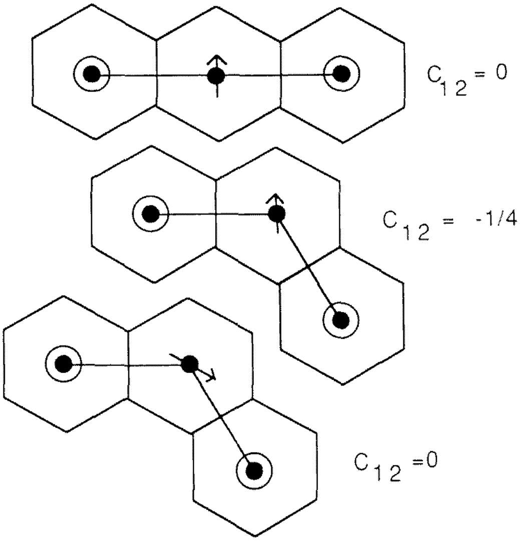

Fig. 4. Matrix elements for red v_2 vectors.

These are illustrated in fig. 4. The red vertices 1 and 2 are encircled. The vertical direction is indicated for one ring, but is the same for all. As for E, the easiest situation is when the whole set has linear connections so that the matrix C is diagonal with 1 for each eigenvalue. The vertical direction can be chosen to assist this. Thus, using the previous v_1 set and this v_2 set alone, we can then deduce that at least $2R$ values of A are greater than or equal to 1.

Similarly, the vectors v_3 over the red set give the matrix D_{rs} with matrix elements:

$$\begin{aligned} D_{rs} &= 1, && r = s; \\ &= 0, && \text{if } r \text{ and } s \text{ separated by a straight line;} \\ &= -1/3, && \text{if } r \text{ is a second neighbour vertically above } s; \\ &= -1/12, && \text{if an angular connected second neighbour;} \\ &= 0, && \text{if more distant.} \end{aligned}$$

Since D has more non-zero interactions than C, it is less easy to use and often gives less information. Furthermore, when both these sets of vectors are used, it is possible that there will be matrix elements between the two sets of vectors though not between those on the same hexagon. The lowest eigenvalue L of the combined matrix of which C and D are diagonal blocks is needed. This L is the lower bound such that there are at least $3R$ eigenvalues of A greater than L. Any matrix elements of A between these vectors and the v_1 vectors may be ignored because the difference of 1 between their diagonal elements means that their effect is very small.

For an alternant molecule, there is the mirror property that each strictly positive eigenvalue has a corresponding strictly negative one which is its negative. The information about the distribution of positive eigenvalues of A is then balanced by information about its negative eigenvalues.

8. The effect of other rings

The complication of having other-sized rings among the hexagons can be dealt with by the same arguments. There will always be an eigenvector υ for any ring with the eigenvalue 2. It gives all the atoms around the ring equal components. It is used in place of υ_1 when the ring belongs to the red set. The rest of the argument for the eigenvalues greater than or equal to 2 is very similar, although the matrix elements between rings and hexagons and rings and rings are more varied. In general, it is desirable to include the ring in the red set if it has fewer than six atoms, since such a ring is less effective in separating two red hexagons. Thus, the red set is defined for a larger class of molecule but its use is confined to the upper eigenvalues. The lower eigenvalues can be discussed by embedding ethene to find the white number.

9. Examples

The utility of these results is seen more clearly by showing how they apply to some examples.

For the polyacenes, being linear catacondensed molecules, the red set will have $R = r/2$ if r is even and $R = (r + 1)/2$ if r is odd, i.e. the red set contains every other ring starting from one end. These vertices are all in the same line so the matrix E consists of 2 along the diagonal, and so the number of eigenvalues greater than or equal to 2 is at least R. In fact, since there are explicit formulae for these eigenvalues [8], we know that this is exactly the number of these eigenvalues. Similarly, using all three vectors with the vertical taken normal to the bual edges, the number of eigenvalues greater than or equal to 1 is at least $3R$. The remaining positive eigenvalues are generally less than 1 in magnitude.

Another series of catacondensed molecules which can be treated simply has its rings placed alternatively to one side and to the other of a central axis, as in chrysene. In this, the matrix elements of E between alternate rings are 1/6. The lowest eigenvalue of this E for any number of rings is always greater than $2 - 1/3 = 1.666$. In fact, for $r = 3$, the eigenvalue of E is 1.833. By using A twice, the bound for $r = 3$ is raised to 1.915 and, for large r, this bound is 1.826 so that tighter bounds can be found for these molecules. The number of eigenvalues of A greater than 1.826 is then at least $R = r/2$ for r even and $(r + 1)/2$ for r odd. The actual results are shown in table 1. By selecting vertices which are at least two hexagons apart so that all the interactions vanish, further information about the number strictly greater than or equal to 2 is obtained. Similarly for the lower eigenvalues. By taking the vertical direction of v_2 along the axis of the molecule, C is diagonal and the theorem shows that the number of eigenvalues greater than or equal to 1 will be at least $2R$. The use of v_3 and D allows the result to be extended to show that there are at least $3R$ greater than 0.33. Alternatively, by taking fewer and more distant vertices with v_3, W, the number greater than or equal to 1, can be estimated. This technique of using a selection of v_2 and v_3 vectors is generally more efficient for polyhex than the embedding of ethene fragments used earlier for polyenes. The actual results for this series is shown in table 2.

Table 2

Eigenvalues of the chrysene series of molecules in various ranges. r is the number of rings, R is the red number, W is the white number.

r	R	$\#(\varepsilon \geq 1.83)$	W	$\#(\varepsilon \geq 1)$	$\#(\varepsilon \geq 1/3)$
2	1	1	3	4	5
3	2	2	5	5	7
4	2	2	6	6	9
5	3	3	8	8	11
6	3	3	8	10	13
7	4	4	10	11	15
8	4	5	11	12	17
9	5	5	13	13	19
10	5	5	13	15	21

Table 2 shows that the R is always less than or equal to the next column giving the number of eigenvalues greater than 1.83. The fourth column W is always less than or equal to the fifth column and the sixth is greater than $3R$. Since none of these molecules listed has an eigenvalue less than 1/3, the final column is also the total number of positive values, so that the theorem adds nothing here. Clearly, the theorem is always obeyed! It can be seen that the first condition, using R, is the most useful in this series since the bound is often the exact number of eigenvalues and the condition embodied in W is the next most useful.

10. Extension to non-alternants

The above application can be interpreted as an approximate embedding using hexagons. The embedding of hexagons is facilitated by using the bual. The theorem can also be applied to the original adjacency matrix A without using the bual but by taking some other fragment to embed. Thus, as a simple example, we can take as the vector a one-component vector on one atom. This methyl fragment has a zero eigenvalue. The related independent set is then defined as an independent set of C atoms. For an alternant, its size N is $n/2$ or $(n+1)/2$ for n even or odd, respectively (i.e. $N = \lfloor (n+1)/2 \rfloor$), where n is the number of C atoms. For a non-alternant, at least three colours are needed and the red set will be the largest independent set of C atoms. An odd numbered ring with $2n+1$ atoms will have $N = n$. These vectors have zero mean values so the diagonal elements of E are zero, and since none of the neighbouring atoms are in the set, the off-diagonal elements are also zero. The theorem then states that there are at least N eigenvalues which are positive (or zero) and at least N which are negative (or zero). For an odd alternant, this allows us to conclude that at least one eigenvalue will be zero. For a non-alternant, it gives some more interesting information on the balance between positive and negative eigenvalues. Thus, heptafulvalene ($n = 14$) has $N = 6$, so it is not surprising that one of its occupied orbitals has a negative eigenvalue.

Since every ring has 2 as an eigenvalue, more progress can be made on the larger eigenvalues of molecules containing rings than on the smaller ones. By counting R, the number of independent red rings, irrespective of size, a bound to the number of eigenvalues greater than or equal to 2 is obtained. Similarly, by embedding the maximum number of ethene fragments W, the bound to the total number greater than or equal to 1 is obtained. Some examples of these relations are given in table 3, which shows that the bounds are always close to the actual numbers of the eigenvalues. Where the numbers differ in the two last columns, it is interesting that the smallest eigenvalue involved is exactly equal to 1.

Table 3

Distribution of eigenvalues for non-alternants.

Molecule	R	$\#(e \geq 2)$	W	$\#(e \geq 1)$
fulvene	1	1	2	2
acenaphthylene	1	1	4	4
fluoranthrene	2	2	5	6
pentalene	1	1	2	3
azulene	1	1	3	3
pyracylene	2	2	5	5
fulvalene	1	1	3	3

11. Relations for the total pi energy

It is possible to consider dividing a molecule into two disjoint parts and summing the energies of these to obtain an estimate of the energy of the molecule. We can now examine this relation using the Rayleigh theorem.

If the vectors to be used for E are the occupied molecular orbitals of the two molecular fragments, then E will have their energies on its diagonal. There will be off-diagonal elements between the orbitals of the two fragments but these have no effect on the trace of E, which gives an estimate of the total energy. Thus, the sum of the energies of the two fragments will approximate the total energy but, because the eigenvalues of E are less than those of A, the estimate will always be an underestimate.

A better estimate can be found by dividing the molecule into two radical fragments. The same argument can be applied. However, each radical has a non-bonding orbital with $e = 0$. These two will interact in E because of the bonds between the fragments. This interaction is easily calculated because the non-bonding orbital can be found without reference to the remaining eigenvectors. The consequence of the interaction is that their energy is split. One eigenvector becomes occupied by two electrons, while the other is empty. Thus, the trace of E is no longer the total energy. The repulsive energy of the empty orbital (viz. the interaction) must be removed and this increases the estimate of the total energy. The result is still an underestimate of the total energy since the other occupied orbitals have some interaction with the empty eigenvectors not in the basis of E.

There are many ways of dividing a molecule into fragments. Evidence from a small number of examples suggests that it may be an advantage if the least number of bonds are broken in doing this. It may also be an advantage to minimize the number of atoms with one C neighbour.

As an example, we consider the division of anthracene. It can be divided symmetrically into two benzyl radicals. These interact at two points and their interaction is 5/7. One of the combined molecular orbitals has an energy of 5/7 and the other of −5/7. The former becomes doubly occupied and the latter empty. The sum of the radical energies is to be corrected by 10/7 to allows for this. The total now becomes $2(8.72057) + 10/7 = 18.86971$. A slightly different estimate is obtained by using β-naphthyl-methyl and allyl radicals. These give 18.62734. Since the correct value is 19.31371, neither is very close.

The reason for this lack of accuracy is the fact that several connecting bonds have been removed in the division. Since the sum of the squares of the occupied energies of an alternant is the total number of CC bonds, it follows that removing several bonds does damage to the set of eigenvalues by reducing them and so the total pi energy must be reduced. The radical device is a partial accounting for this lack.

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Appendix

Since the colouring of a graph consisting of triangles is unfamiliar, it is of interest to comment on some results. The triangle requires three colours, since no two of its vertices can have the same colour. The largest possible value of R, the size of the independent red set, equals the number of triangles. Each of the red vertices then belongs to one triangle. A first step in selecting the red vertices is to look at those which belong to one triangle. Vertices belonging to two triangles should be examined next. If the triangles which contain the red vertices are not all the triangles, then it is worth while to try to enlarge the selection. Those belonging to many triangles are the least desirable.

References

[1] I. Gutman and G.G. Hall, Int. J. Quant. Chem. 41(1992)667.

[2] Lord Rayleigh, *The Theory of Sound*, 2nd Ed. (Dover, New York, 1945);
S.H. Gould, *Variational Methods for Eigenvalue Problems* (Oxford University Press, Oxford, 1966).

[3] G.G. Hall, Trans. Faraday Soc. 53(1957)573; Mol. Phys. 33(1977)551.

[4] J.R. Dias, J. Chem. Educ. 64(1987)213.

[5] E. Bodewig, *Matrix Calculus* (North-Holland, Amsterdam, 1959).

[6] R.G. Busacker and T.L. Saaty, *Finite Graphs and Networks* (McGraw–Hill, New York, 1965).

[7] G.G. Hall, Int. J. Math. Educ. Sci. Tech. 4(1973)233; Theor. Chim. Acta 73(1988)425.

[8] C.A. Coulson, J. Phys. Soc. London 60(1948)257.