

Commentationes

The Electronic Structure of the Boron Hydrides

Part III. Basic Theory and its Relationship to the Hückel Theory of Conjugated Hydrocarbons

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In parts I and II of this series [1] it has been demonstrated that localized three centre and two centre bonds may be used as basic functions for molecular orbital calculations on closed ("cage") and open ("basket") boron polyhedral molecules. In the present paper it is shown that the "face" and "edge" matrices of this theory are related to incidal and 1 and 2 simplexial matrices in the same way that Hückel matrices in the theory of unsaturated hydrocarbons are related to incidal matrices and 0 and 1 simplexial matrices. The theory is thus a topologically-correct extension of Hückel theory to three dimensions.

In Teil I und II dieser Serie [1] wurde demonstriert, daß lokalisierte Dreizentren- und Zweizentren-Bindungen als Basisfunktionen für MO-Rechnungen bei geschlossenen („Käfig“) und offenen („Korb“) polyhedralen Borwasserstoff-Molekülen benutzt werden können. In der vorliegenden Arbeit wird gezeigt, daß die „Oberflächen“- und „Randmatrizen“ dieser Theorie mit Incidal- sowie 1- und 2-Simplexmatrizen verwandt sind, in derselben Art wie die Hückel-Matrizen in der Theorie der ungesättigten Kohlenwasserstoffe mit Incidal-Matrizen sowie 0- und 1-Simplexmatrizen in Beziehung stehen. Die Theorie ist somit eine topologisch korrekte Erweiterung der Hückel-Theorie auf drei Dimensionen.

Dans les parties I et II de cette suite d'articles on a démontré que des liaisons localisées à trois et à deux centres peuvent être employées comme fonctions de base pour des calculs d'orbitales moléculaires sur des molécules polyédriques boriques fermées («cage») et ouvertes («panier»). Dans cet article on montre que les matrices «faces» et «arêtes» de cette théorie sont liées aux matrices d'incidence et aux matrices simplexes 1 et 2 de la même manière que dans la théorie de Hückel la matrice hamiltonienne est reliée aux matrices d'incidence et simplexes 0 et 1. La théorie est donc une extension à trois dimensions, correcte du point de vue topologique, de la méthode de Hückel.

The inorganic chemist has for many years rationalised the electronic structure of the polyhedral boron hydrides in terms of three-centred bonds [2]. Two classes of three-centre bonds have been invoked, nodeless and single-noded. Examples of the first class are shown in Figs. 1 and 2, which depict, respectively, $B \begin{array}{c} \diagup H \diagdown \\ \diagdown \quad \diagup \end{array} B$ and $B \begin{array}{c} \diagup B \diagdown \\ \diagdown \quad \diagup \end{array} B$ three centred bonds. The second class is exemplified in Fig. 3 by a $B \begin{array}{c} \diagup B \diagdown \\ \diagdown \quad \diagup \end{array} B$ bond. It is a simple matter to justify the use of such localised orbitals for each of these groups, but the justification for their use in more delocalised systems rests upon the fact that their use usually leads to a correct count of the number of bonding orbitals. There are difficulties, however. For example, the octahedral

$B_6H_6^{2-}$ anion, with eight equilateral triangles of boron atoms (Fig. 2), has fourteen, not sixteen, electrons associated primarily with the cage bonding. Further, for molecules containing "basket" arrangements of boron atoms (i.e. fragments of polyhedra) it is necessary to require that two boron atoms bridged by a hydrogen (Fig. 1) do not participate in a bond of the type shown in Fig. 2, although X-ray measurements indicate that the two boron atoms may be closer together than others which are considered to participate in $B \begin{array}{c} \nearrow B \\ \searrow \end{array} B$ bonding.

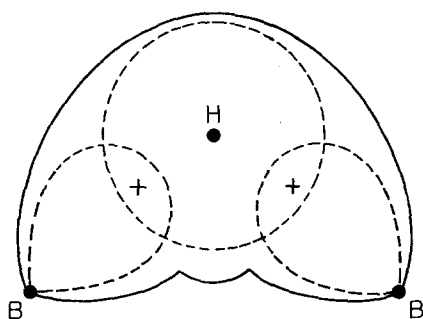


Fig. 1

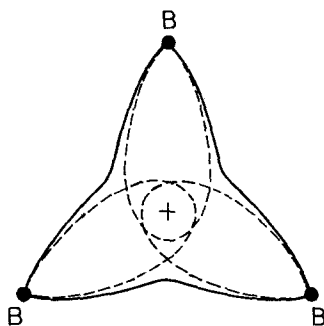


Fig. 2

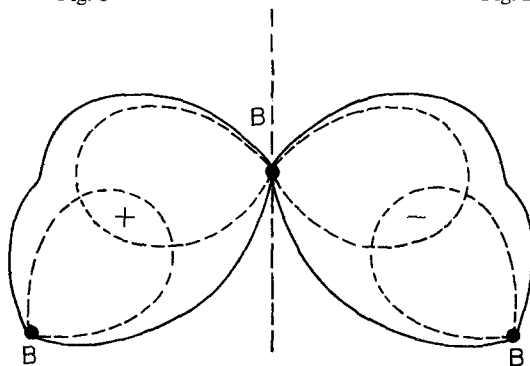


Fig. 3

In Parts I and II of this series we showed that these difficulties could be removed by recognition of non-orthogonality between members of the basis of three-centred localised orbitals. As a first approximation, the problem was treated in Hückel fashion, a localized three centre orbital being assigned a coulomb energy α' , all resonance integrals being set equal to zero, except those between orbitals which correspond to polyhedra faces with an edge in common, which were given the value β' . Such calculations led to a delocalised molecular orbital energy level scheme similar to those obtained from more extended molecular orbital calculations. As an example, we compare in Table 1 the results of our calculations for the $B_6H_6^{2-}$ octahedron using a basis of localised orbitals of the type shown in Fig. 2 – "face" orbitals – with those of Longuet-Higgings and Roberts [3].

The use of a topological basis set corresponding to triangular faces of a boron polyhedron was suggested by the success obtained for metal-metal bonded systems. This latter application also suggested that it might be profitable to consider a basis

corresponding to polyhedron edges. That is, of localised, two-centre (“edge”) orbitals. Such calculations were carried out, the coulomb integrals being given the value α , and resonance integrals between bonds which corresponded to sides bounding the same triangular polyhedron face were given the value β . All other resonance integrals were set equal to zero. These calculations show that if the energy of a molecular orbital of a closed polyhedron using the “face” basis is $\alpha' + n\beta'$, the corresponding molecular orbital using the “edge” basis is $\alpha + (n + 1)\beta'$. Orbitals unique to either set have energies $\alpha - 3\beta$ (“face” basis) or $\alpha' - 2\beta'$ (“edge” basis) (results for the “edge” basis are also included in the Table). These generalisations, however, do not apply to the “basket” boron hydrides.

Table

Molecular orbital symmetry		Orbital energies		
		“edge” basis	“face” basis	Ref. [3]
unoccupied	A_{2u}		$\alpha' - 3\beta'$	
molecular	E_g	$\alpha - 2\beta$		$-0.88x^a$
orbitals	T_{2u}	$\alpha - 2\beta$		$-0.42x$
occupied	T_{2g}	α	$\alpha' - \beta'$	$0.49x$
molecular	T_{1u}	$\alpha + 2\beta$	$\alpha' + \beta'$	$1.02x$
orbitals	A_{1g}	$\alpha + 4\beta$	$\alpha' + 3\beta'$	$2.97x$

^a The parameter x is, very roughly, a linear function of energy.

In the present paper we discuss the origin of these relationships and demonstrate that the bases and method of calculation which we have used are a topologically-correct extension of Hückel theory to three dimensional systems. We do this by demonstrating the isomorphism which exists between our Hückel matrices and certain topological matrices, which are themselves inter-related. Precisely similar relationships hold for the Hückel matrices used to describe conjugated hydrocarbons and similar molecules.

First, we introduce some of the nomenclature of topology. A 2-simplex is associated with an equilateral triangle, a 1-simplex with a line and a 0-simplex with a point [4]. The analogy which exists between 2-, 1- and 0-simplexes and “face”, “edge” and atomic orbital bases should be apparent. The arguments which we present are most clearly demonstrated by a detailed consideration of particular cases, but we shall introduce generalizations where appropriate.

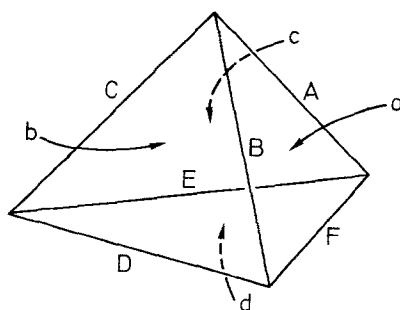


Fig. 4

Consider a tetrahedral array of 0-simplexes (Fig. 4), the associated 1- and 2-simplexes being labelled as indicated. The 2,-2-simplexial matrix is

$${}^2\mathbf{S} = \begin{matrix} & a & b & c & d \\ \begin{matrix} a \\ b \\ c \\ d \end{matrix} & \begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix} \end{matrix} \quad (1)$$

Similarly, the 1-, 1-simplexial matrix is

$${}^1\mathbf{S} = \begin{matrix} & A & B & C & D & E & F \\ \begin{matrix} A \\ B \\ C \\ D \\ E \\ F \end{matrix} & \begin{bmatrix} 0 & 1 & 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & 1 & 1 & 0 \end{bmatrix} \end{matrix} \quad (2)$$

Consider the non-polarized 1-, 2-incidence matrix¹

$${}^{1,2}\mathbf{I} = \begin{matrix} & A & B & C & D & E & F \\ \begin{matrix} a \\ b \\ c \\ d \end{matrix} & \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix} \end{matrix} \quad (3)$$

Form the products ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$ and ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$, where \mathbf{I}^{tr} is the transpose of the matrix \mathbf{I}

$${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}} = \begin{bmatrix} 3 & 1 & 1 & 1 \\ 1 & 3 & 1 & 1 \\ 1 & 1 & 3 & 1 \\ 1 & 1 & 1 & 3 \end{bmatrix}, \quad (4)$$

$${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I} = \begin{bmatrix} 2 & 1 & 1 & 0 & 1 & 1 \\ 1 & 2 & 1 & 1 & 0 & 1 \\ 1 & 1 & 2 & 1 & 1 & 0 \\ 0 & 1 & 1 & 2 & 1 & 1 \\ 1 & 0 & 1 & 1 & 2 & 1 \\ 1 & 1 & 0 & 1 & 1 & 2 \end{bmatrix} \quad (5)$$

The elements in ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$ count the number of 1-simplexes which the 2-simplexes have in common; similarly the elements in ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ count the number of 2-simplexes which the 1-simplexes, taken in pairs, together bound. It is evident that, if

¹ The more usual (polarized) incidence matrix would appear appropriate to a discussion based on antibonding orbitals as basis.

${}^{1,2}\mathbf{I}$ is an $m \times n$ matrix with $m > n$, then

$${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}} = {}^2\mathbf{S} + 3\mathbf{1}_n \quad (6)$$

where $\mathbf{1}_n$ is a $n \times n$ unit matrix and

$${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I} = {}^1\mathbf{S} + 2\mathbf{1}_m. \quad (7)$$

Relations (6) and (7) are true for all polyhedra composed of equilateral triangular faces (Part I).

Now ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ and ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$ are of the same rank, (r) ($= 4$ in the example above), although ${}^1\mathbf{S}$ and ${}^2\mathbf{S}$ will in general not be (${}^1\mathbf{S}$ is of rank 4 and ${}^2\mathbf{S}$ of rank 3 in the example above), and will have r identical eigenvalues, from the general rule that if \mathbf{A} is an $n \times m$ matrix and \mathbf{B} is an $m \times n$ matrix, \mathbf{AB} and \mathbf{BA} have the same rank r and they have r identical eigenvalues [5].

From the definition of rank it follows that all other eigenvalues will be zero. As is evident from (6) and (7), the eigenvalues of ${}^1\mathbf{S}$ and ${}^2\mathbf{S}$ are closely related to those of ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ and ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$; corresponding eigenvalues will differ by unity, the others having a value of -3 for ${}^2\mathbf{S}$ and -2 for ${}^1\mathbf{S}$. Now, in our discussion of the B_4 tetrahedron we set up "face" and "edge" matrices which are isomorphous with ${}^2\mathbf{S}$ and ${}^1\mathbf{S}$ respectively. The origin of the relationships between the eigenvalues obtained from the "face" and "edge" secular determinants follows immediately from this isomorphism.

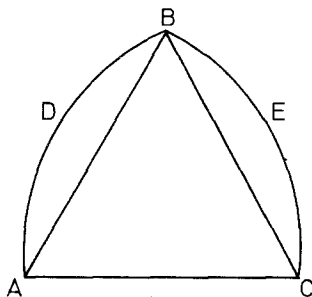


Fig. 5

For "basket" polyhedra, although ${}^1\mathbf{S}$ is related to ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ and ${}^2\mathbf{S}$ to ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$, relationships (6) and (7) are no longer valid. Consider the example shown in Fig. 5, where the symbolism of Part II is followed. Corresponding to bases ii) and iv) Part II, in which B-H-B bridges are included and set equivalent to a B-B-B triangle and B-B bond, respectively, we have

$${}^1\mathbf{S} = \begin{array}{c} AB \\ BC \\ CA \end{array} \begin{array}{ccc} AB & BC & CA \\ \left[\begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array} \right] \end{array} \quad (8)$$

$${}^2\mathbf{S} = \begin{array}{c} ABD \\ BCE \\ ABC \end{array} \begin{array}{ccc} ABD & BCE & ABC \\ \left[\begin{array}{ccc} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{array} \right] \end{array} \quad (9)$$

and

$$\begin{array}{c}
 \begin{array}{ccc}
 & AB & BC & CA \\
 ABD & \left[\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 1 \end{array} \right] \\
 {}^{1,2}\mathbf{I} = BCE \\
 ABC
 \end{array}
 \end{array} \quad (10)$$

so that

$${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I} = \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (11)$$

$${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & 1 & 3 \end{bmatrix} \quad (12)$$

Although the "face" and "edge" matrices are isomorphous with ${}^2\mathbf{S}$ and ${}^1\mathbf{S}$ respectively, these latter are no longer simply related to the products of the incidence matrix with its transpose. However, comparison of (1) and (4), (2) and (5), (8) and (11), and (9) and (12) indicates the general rule:

${}^1\mathbf{S}$ may be formed from ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ and ${}^2\mathbf{S}$ from ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$ by deletion of the diagonal elements of the product incidence matrices.

It may be shown for all of the examples discussed in Part II that by the introduction of suitable terms in the diagonal of ${}^1\mathbf{S}$ and ${}^2\mathbf{S}$ that a correspondence of eigenvalues can be obtained, similar to that found in Part I. It may be noted that zero-valued eigenvalues will still be obtained corresponding to the nullity of ${}^1\mathbf{S}$ and ${}^2\mathbf{S}$; this feature may be seen in the results reported in Part II, although we did not then comment upon it. It should further be noted that those diagonal elements of ${}^{1,2}\mathbf{I}^{\text{tr}} {}^{1,2}\mathbf{I}$ and ${}^{1,2}\mathbf{I} {}^{1,2}\mathbf{I}^{\text{tr}}$ for "basket" polyhedra which have unique values correspond to unique simplexes (*cf.* ABC with ABD and BCE in the example above); and it is to the corresponding diagonal terms in ${}^1\mathbf{S}$ and ${}^2\mathbf{S}$ that one would make corrections to allow for simplex uniqueness.

The Hückel Theory of Conjugated Hydrocarbons

It is recognised that many results derived from the Hückel approach to conjugated hydrocarbons is a consequence of the isomorphism between the Hückel and the so-called "topological" matrix. We shall conclude this paper by demonstrating that the topological (or Hückel) matrix is itself derived from an incidence matrix by a rule analogous to that given earlier. It follows, therefore, that our work is a topologically correct generalization of Hückel theory to three dimensional systems.

We consider two familiar examples; the benzene molecule and the allyl radical, which are the two dimensional analogous of the closed (cage) and open (basket) polyhedra discussed earlier.

The Benzene Molecule

Using the notation of Fig. 6 we construct 0-, 0-simplexial and 1-, 1-simplexial matrices

$${}^0\mathbf{S} = \begin{array}{c} \begin{array}{cccccc} & A & B & C & D & E & F \\ A & 0 & 1 & 0 & 0 & 0 & 1 \\ B & 1 & 0 & 1 & 0 & 0 & 0 \\ C & 0 & 1 & 0 & 1 & 0 & 0 \\ D & 0 & 0 & 1 & 0 & 1 & 0 \\ E & 0 & 0 & 0 & 1 & 0 & 1 \\ F & 1 & 0 & 0 & 0 & 1 & 0 \end{array} \end{array} \quad (13)$$

$${}^1\mathbf{S} = \begin{array}{c} \begin{array}{cccccc} & a & b & c & d & e & f \\ a & 0 & 1 & 0 & 0 & 0 & 1 \\ b & 1 & 0 & 1 & 0 & 0 & 0 \\ c & 0 & 1 & 0 & 1 & 0 & 0 \\ d & 0 & 0 & 1 & 0 & 1 & 0 \\ e & 0 & 0 & 0 & 1 & 0 & 1 \\ f & 1 & 0 & 0 & 0 & 1 & 0 \end{array} \end{array} \quad (14)$$

These matrices are isomorphic with each other and the Hückel matrix.

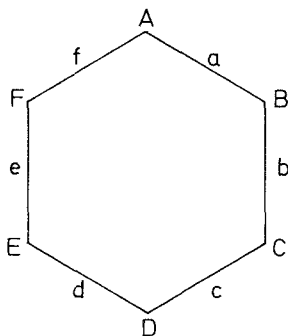


Fig. 6

The 0-, 1-non-polarized incidence matrix is

$${}^{0,1}\mathbf{I} = \begin{array}{c} \begin{array}{cccccc} & A & B & C & D & E & F \\ a & 1 & 1 & 0 & 0 & 0 & 0 \\ b & 0 & 1 & 1 & 0 & 0 & 0 \\ c & 0 & 0 & 1 & 1 & 0 & 0 \\ d & 0 & 0 & 0 & 1 & 1 & 0 \\ e & 0 & 0 & 0 & 0 & 1 & 1 \\ f & 1 & 0 & 0 & 0 & 0 & 1 \end{array} \end{array} \quad (15)$$

It is readily shown that

$${}^{0,1}\mathbf{I}^{\text{tr}} {}^{0,1}\mathbf{I} = {}^{0,1}\mathbf{I} {}^{0,1}\mathbf{I}^{\text{tr}} = \begin{bmatrix} 2 & 1 & 0 & 0 & 0 & 1 \\ 1 & 2 & 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 1 & 0 & 0 \\ 0 & 0 & 1 & 2 & 1 & 0 \\ 0 & 0 & 0 & 1 & 2 & 1 \\ 1 & 0 & 0 & 0 & 1 & 2 \end{bmatrix} \quad (16)$$

so that ${}^{0,1}\mathbf{I}^{\text{tr}} {}^{0,1}\mathbf{I} = {}^{0,1}\mathbf{I} {}^{0,1}\mathbf{I}^{\text{tr}} = {}^0\mathbf{S} + 1\mathbf{I}_6 = {}^1\mathbf{S} + 1\mathbf{I}_6$. The topological similarity between a cage molecule and a cyclic conjugated system is seen by comparing these relationships with Eqs. (6) and (7).

The Allyl Radical

Using the notation of Fig. 7 we construct 0-, 0- and 1-, 1-simplexial matrices

$${}^0\mathbf{S} = \begin{array}{c} A \quad B \quad C \\ A \\ B \\ C \end{array} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad (17)$$

$${}^1\mathbf{S} = \begin{array}{c} a \quad b \\ a \\ b \end{array} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (18)$$

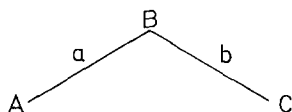


Fig. 7

The 0-, 1-non-polarized incidence matrix is

$${}^{0,1}\mathbf{I} = \begin{array}{c} A \quad B \quad C \\ a \\ b \end{array} \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \end{bmatrix} \quad (19)$$

so that

$${}^{0,1}\mathbf{I}^{\text{tr}} {}^{0,1}\mathbf{I} = \begin{bmatrix} 1 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 1 \end{bmatrix} \quad (20)$$

and

$${}^{0,1}\mathbf{I} {}^{0,1}\mathbf{I}^{\text{tr}} = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix} \quad (21)$$

The topological analogy between basket polyhedra and non-cyclic conjugated hydrocarbon systems may be seen by comparing, in particular (8) and (11) with (17) and (20). In each pair, the differences occur along the leading diagonal of the matrices.

Comparison of (13) and (14) with (16), of (17) with (20), and of (18) with (21) indicates the general rule:

0S may be formed from ${}^{0,1}I^{tr}$, ${}^{0,1}I$ and 1S from ${}^{0,1}I$, ${}^{0,1}I^{tr}$ by deletion of the diagonal elements of the product incidence matrices.

This rule demonstrates that the topological origin of the Hückel matrix of conjugated planar systems, which is isomorphous with 0S ,² lies in the 0-, 1-incidence matrix. We have already demonstrated that the calculations which we have carried out on polyhedral molecules are similarly related to the 1-, 2-incidence matrix. Our calculations are therefore a topologically-correct extension of Hückel theory to three dimensional molecules.

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² Although the matrix 1S is not generally discussed it should be noted that its eigenvalues map into those of 0S .