Molecular orbitals and Hadamard matrices

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The orthogonal set of molecular orbitals can be constructed from Hadamard matrices. The nodal properties of molecular orbitals can be inferred from the sign changes in the rows of Hadamard matrices. Number of inequivalent sets of orthogonal MOs is given by the number of equivalence classes of Hadamard matrices.

1. Introduction

Qualitative description of molecular orbitals and their nodal properties go back to the work of Wilson [1] and others [2,3]. It is well known that the number of nodes in a MO determines the energy order of the molecular orbital. There are several computational packages based on ab initio and other methods which yield the desired accuracies for the energies of molecular orbitals. Yet it is necessary and important to know the qualitative nature, shapes and nodal properties of molecular orbitals. In addition to aesthetic and mathematical appeal such qualitative analysis can be extremely useful for a priori prediction of orbital energy ordering and to provide insight into the nature of bonding in such species.

King [4–6] has extensively employed simple MO techniques to obtain topological properties of metal clusters. Such techniques combined with electron count procedures appear to provide novel insights into relative stabilities of different molecular topologies of inorganic clusters. This combined with the recent intense activity in topological properties of fullerene clusters call for the development of techniques which yield insight into the nature of molecular orbitals.

A general question that may be asked is how many topologically inequivalent sets of N orthogonal MOs can be constructed for a system containing N vertices (N atoms)? The answer is not obvious and in fact it is not even evident that there should be two inequivalent sets of N orthogonal MOs for a system containing N atoms. By inequivalent sets we mean MO sets having different nodal properties and yet all MOs within a given set maintain the required orthogonality criterion. In this Letter, we seek an answer to this question for systems which contain N = 4m vertices through Hadamard matrices [7–16]. Hadamard matrices are matrices containing 1s and -1s such that any two rows in the matrix are orthogonal. These matrices have been extensively employed in combinatorial designs [7–12]. Construction of Hadamard matrices has received considerable attention from the mathematical community [7–12]. As a result there are several procedures and theorems to construct Hadamard matrices. Hadamard matrices also find important applications in Hadamard transform spectroscopy [7,14–16]. As demonstrated by the author [17,18] huge amounts of computer time need to be spent in search of Hadamard matrices.

The relation between Hadamard matrices and molecular orbitals has not been studied at all. This is the first study which reveals that indeed there is an important connection and that there are inequivalent sets of MOs with different nodal properties for a system containing N vertices, in general. The objective of this Letter is to establish such a connection and show the existence of topologically inequivalent sets of orthogonal MOs, in general.
2. Hadamard matrices

An \( n \times n \) square matrix \( H \) composed of 1s and \(-1\)s is said to be a Hadamard matrix if

\[
HH^T = H^TH = nI,
\]

where \( I \) is the \( n \times n \) identity matrix and \( H^T \) is the transpose of the matrix \( H \). Note that the rows of the Hadamard matrices as vectors in a \( n \)-dimensional vector space are orthogonal to each other. This is precisely the reason that Hadamard matrices are useful in several applications including Hadamard transform spectroscopy.

As an example consider the following \( 4 \times 4 \) matrix,

\[
H_4 = \begin{pmatrix}
1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 \\
1 & 1 & -1 & -1 \\
1 & -1 & -1 & 1
\end{pmatrix}.
\]

The constraint that the Hadamard matrices should have only +1s and -1s leads to the result that with the exception of \( 1 \times 1 \) and \( 2 \times 2 \) Hadamard matrices all Hadamard matrices must be of order \( n \times n \) such that \( n = 4m \) for some integer \( m \). There exists Skew-Hadamard matrices \( H = S + I \), where \( S \) is a Skew-symmetric matrix with 1s and -1s such that

\[
S_{ij} = -S_{ji}.
\]

Note that the rows of the Skew–Hadamard matrices are also orthogonal. The Skew–Hadamard matrices can be constructed using a theorem due to Williamson [12] this method was computerized by the author [18] recently for exhaustive generation of Skew–Hadamard matrices. Regular Hadamard matrices can be constructed from Skew–Hadamard matrices as seen in the expository article of Wallis et al. [12].

There are several techniques for the construction and characterizations of Hadamard matrices. The author [17] has recently considered techniques to characterize Hadamard matrices based on smallest binary codes and the characteristic polynomials. Interested readers can find further details in ref. [17].

Two Hadamard matrices \( H_1 \) and \( H_2 \) are considered equivalent if there exist monomial permutation matrices composed of 1's and \(-1\)'s such that

\[
H_2 = PH_1Q.
\]

The above relation is tantamount to defining two Hadamard matrices \( H_1 \) and \( H_2 \) to be equivalent if one is obtainable from the other by (a) a permutation of the rows, (b) a permutation of the columns, (c) multiplication of any row or column by \(-1\), and (d) any combination of operations, (a)–(c). The above definition of equivalence parallels quantum-chemical equivalence of molecular orbitals. For example, two MOs are the same if they differ simply by a sign. Permutation of rows of the matrices merely correspond to relabeling of molecular orbitals. The beauty of the above equivalence relation is that under this operation the overall sign of an MO may change, MOs may be relabeled but the overall nodal properties of the MOs must be preserved for a given system.

Suppose that the rows of the Hadamard matrices are imagined as orthogonal combination of AOs to yield MOs. If there exist inequivalent Hadamard matrices then we would have inequivalent sets of orthogonal MOs. Section 3 considers this important question.

3. Molecular orbitals and Hadamard matrices

The Hadamard matrix \( H_4 \) considered in section 2 can be envisaged to yield the following four orthogonal MOs for butadiene, cyclobutadiene or the four valence MOs of the \( Li_4 \), \( Au_4 \) clusters and so on, but for normalization constants which can be readily incorporated. The matrix \( H_4 \) in eq. (2) is equivalent to the matrix \( H'_4 \) shown as

\[
H'_4 = \begin{pmatrix}
1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 \\
1 & 1 & -1 & -1 \\
1 & -1 & -1 & 1
\end{pmatrix},
\]

which yields the MOs shown as

\[
\psi_1 = (\phi_1 + \phi_2 + \phi_3 + \phi_4), \quad (6)
\]
\[
\psi_2 = (\phi_1 + \phi_2 - \phi_3 - \phi_4), \quad (7)
\]
\[
\psi_3 = (\phi_1 - \phi_2 - \phi_3 + \phi_4), \quad (8)
\]
\[
\psi_4 = (\phi_1 - \phi_2 + \phi_3 - \phi_4). \quad (9)
\]

That is, the four rows of \( H'_4 \) in the same order yield the well-known set of four MOs of butadiene, cyclo-
butadiene etc. The relative ordering of these MOs would of course depend on the connectivity of the atoms and the nodal properties which result from the connectivity. For butadiene the four rows of \( H_4 \) yield the nodal pattern \((0, 1, 2, 3)\) where the \( i \)th component of the ordered-tuple is the number of nodes in the \( i \)th MO. While the same four rows of \( H_4 \) yield the nodal pattern \((0, 2, 2, 4)\) for cyclobutadiene or \( Li_4 \). Note that the four rows of the \( H_4 \) matrix also constitute the character table of the \( C_{2v} \) group.

As another example let us consider the Hadamard matrix, \( H_8 \) obtained from Sylvester's construction,

\[
H_{2n} = \begin{pmatrix} H_n & H_n \\ -H_n & -H_n \end{pmatrix},
\]

\( H_2 = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \)

\( H_4 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & -1 \end{pmatrix}, \)

\( H_8 = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \end{pmatrix}. \)

The orthogonal MOs corresponding with the above matrix are

\[
\begin{align*}
\psi_1 &= (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_7 + \phi_8), \\
\psi_2 &= (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 + \phi_7 - \phi_8), \\
\psi_3 &= (\phi_1 + \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6 - \phi_7 + \phi_8), \\
\psi_4 &= (\phi_1 - \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6 - \phi_7 + \phi_8), \\
\psi_5 &= (\phi_1 + \phi_2 + \phi_3 + \phi_4 - \phi_5 - \phi_6 - \phi_7 - \phi_8), \\
\psi_6 &= (\phi_1 - \phi_2 + \phi_3 + \phi_4 - \phi_5 - \phi_6 - \phi_7 + \phi_8), \\
\psi_7 &= (\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 + \phi_6 - \phi_7 + \phi_8), \\
\psi_8 &= (\phi_1 - \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 + \phi_7 - \phi_8). \end{align*}
\]

Consequently once the Hadamard matrices are known it is trivial to generate the corresponding orthogonal set of MOs.

The question of the general construction of Hadamard matrices and the construction equivalence classes of Hadamard matrices are open and unsolved problems in general. However for some values of \( n \), the number of inequivalent Hadamard matrices is known. Table 1 summarizes some known results. Hadamard matrices of other orders have been constructed including the recent exhaustive generation of Skew-Hadamard matrices up to order 100 by the author [18]. By the use of computers it is also possible to construct selected larger Hadamard matrices from smaller Hadamard matrices or Skew-matrices using existing algorithms. However, the number of inequivalent matrices for larger matrices is not always known at the present time.

Let us consider the smallest set of Hadamard matrices which contain more than one equivalence class. There are five inequivalent Hadamard matrices of order \( 16 \times 16 \) studied extensively by Hall [8]. Table 2 shows representative matrices from all five of these equivalence classes of Hadamard matrices of order \( 16 \times 16 \). The fifth equivalence class has a representative that is the same as the transpose of the fourth class. The matrices in table 2 are not equivalent in that one is not obtainable from the other by any permutation of rows, columns or by multiplying a row or a column with \(-1\).

Next we consider the nodal properties of the MOs associated with the inequivalent Hadamard matrices. One could visualize the rows of the Hadamard matrices to correspond to the MOs of some linear polymers. This however does not introduce any de-
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Table 2
Five inequivalent Hall's class Hadamard matrices (in the order I, II, III, IV) of order 16. The fifth matrix is the transpose of the fourth matrix.
pendency in the equivalence or inequivalence of the Hadamard matrices as the equivalence depends on the nature of the Hadamard matrices. However, the nodal pattern depends on the connectivity of the vertices in the graph and thus one needs to choose a graph for further discussion. We choose a path of length \( n \) for convenience. The number of nodes in the \( i \)th row of the Hadamard matrix can then be defined as

\[
   n_i = \sum_{j=1}^{n-1} \text{Sgn}(C_{ij}C_{ij+1}) ,
\]

where

\[
   \text{Sgn}(C_{ij}C_{ij+1}) = 1 \quad \text{if} \quad C_{ij}C_{ij+1} > 0 ,
\]

\[
   \text{Sgn}(C_{ij}C_{ij+1}) = -1 \quad \text{if} \quad C_{ij}C_{ij+1} < 0 .
\]

To illustrate the above definition consider the first Hall's Hadamard matrix of order \( 16 \times 16 \). (The first matrix is table 2.) Consider the second row. In moving from left to the right of the matrix consecutively there are two sign changes. Likewise the very last row contains only 1 node but the 12th row in the first matrix in table 2 contains 15 nodes.

We rearrange the rows of the Hadamard matrices with the objective of facilitating a meaningful comparison of different matrices. We arrange the rows such that the number of nodes is in an ascending order. Since the invariance of Hadamard matrices does not depend on such a rearrangement which is tantamount to a permutation of the rows and thus the new Hadamard matrix is related to the old by

\[
   H' = PHQ ,
\]

where \( P \) and \( Q \) are \( n \times n \) permutation matrices. Consequently the two Hadamard matrices are equivalent.

The nodal patterns of five inequivalent Hadamard matrices for paths of length \( n \) arranged according to the number of nodes are shown in table 3. Thus the class 1 Hadamard matrix exhibits the nodal pattern characterized by the vector \((0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15)\) in the sixteen-dimensional space. It is interesting that this nodal pattern corresponds to the sixteen states of a particle in a box problem since for such a system the number of nodes in the state \( n \) is given by \( n - 1 \). All Hadamard matrices in the same equivalence class must have the same nodal pattern for a given graph on \( n \) vertices, although we have not formally proved this. The second equivalence class of \( 16 \times 16 \) Hadamard matrices gives rise to a different nodal pattern \((0, 1, 2, 3, 4, 5, 6, 7, 9, 9, 10, 10, 12, 13, 14, 15)\) as seen from table 3. Evidently the differences are in rows 9, 10, 11 and 12, compared to the first class. The row 9 of the second class has one more node but to compensate row 12 contains one node less.

The third class exhibits the \((0, 1, 2, 3, 4, 5, 6, 7, 9, 10, 10, 11, 11, 12, 14)\) nodal pattern which differs from both the first and second rows. The specific differences are increasing degeneracies in the nodal pat-
Table 3
Nodal patterns for MOs which correspond to the five classes of Hadamard matrices of order $16 \times 16$. The nodal pattern is arranged in an ascending order of the number of nodes.

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Fig. 1 shows the nodal patterns of all four equivalence classes. The energy ordering is approximately determined by the nodal ordering. That is, an MO with more nodes is generally higher in energy compared to an MO with fewer nodes. Therefore Fig. 1 depicts five different ways of constructing molecular orbitals over sixteen orbitals. It is also noteworthy that $16 \times 16$ is the smallest Hadamard matrix exhibiting more than one orthogonal set of topologically inequivalent MOs.

As seen from Table 3, the sum of all the numbers of nodes is the same for all five classes. This result can be mathematically stated as a theorem and in addition we arrive at the following theorems:

**Theorem 1.** The total number of nodes $N = \sum_i n_i$ is the same for all equivalence classes of Hadamard matrices for a given graph.

**Theorem 2.** All Hadamard matrices in an equivalence class as determined by the $H$-equivalence criterion outlined before should have the same nodal-pattern vector for a given graph (arranged in an ascending order of the number of nodes).

**Theorem 3.** The nodal-pattern vectors of two inequivalent Hadamard matrices must be different.

**Theorem 4.** For ordinary non-Skew-Hadamard matrices of order $n = 2^m$ for some integer $m$, the sum of the nodes in all equivalence classes for a path graph is given by

$$N = \sum_i n_i = \frac{1}{2} n (n-1) = \frac{1}{2} (2^m)(2^m - 1) = 2^{m-1}(2^m - 1). \quad (15)$$

The proof for Theorem 4 comes from the Sylvester construction of a Hadamard matrix of order $2^m$:

$$H_2 = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}.$$
For such a Hadamard matrix of order $H_{2n}$ produced by the Sylvester method all rows contain different number of nodes for a linear path graph containing $n$ vertices characterized by the nodal-pattern $(0, 1, 2, ..., 2n - 1)$. Consequently

$$N = \sum_{i} n_i = 0 + 1 + 2 + ... + 2n - 1 = \frac{1}{2}(2n - 1)2n = n(2n - 1). \quad (17)$$

Thus all Hadamard matrices of order $16 (m=4)$ would have a total of

$$2^3(2^4 - 1) = 8(15) = 120 \quad (18)$$

nodes. This is exactly what we find through inspection of the nodal patterns of the five classes of Hadamard matrices shown in table 3.

4. Conclusion

In this Letter, we showed the connection between the orthogonal set of molecular orbitals and Hadamard matrices. It was shown that there are inequivalent ways of constructing orthogonal molecular orbitals with different nodal patterns for a system containing sixteen or more vertices. The nodal patterns were constructed from Hadamard matrices and were analyzed. It was found that the nodal patterns of inequivalent Hadamard matrices were different although the sum of all the number of nodes was found to be invariant for all equivalence classes of Hadamard matrices. Although Hadamard matrices exist only for orders $4m \times 4m$ ($m = \text{integer}$), the construction of orthogonal MOs is certainly possible and feasible for other orders. But the more general question of existence of inequivalent sets of orthogonal MOs over $n$ vertices ($n$ not a multiple of 4) can be answered only through generalization of Hadamard matrices to include irrational matrix elements or redefine these matrices. Such generalizations and properties of the resulting matrices would be the subject of a future publication.

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References