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Proof of the Formulae for the Molecular Orbitals and Energy Levels of Möbius Annulenes, Based on the Theory of Skew-Circulant Matrices

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The formulae for the molecular orbitals and corresponding energy-levels that arise in a Hückel molecular-orbital (HMO) treatment of Möbius systems are derived by appeal to the theory of skew-circulant matrices. The approach adopted is analogous to that previously used to obtain the orbital energies and HMO's of 'Hückel' annulenes from the theory of circulant matrices.

INTRODUCTION

In his classic 1964 paper, Heilbronner[1] stated (without proof) the expressions for the molecular orbitals, and corresponding energy-levels, that arise in a Hückel-molecular-orbital (HMO) treatment of Möbius systems — results which very quickly inspired others[2–9] to an intensive theoretical study of Möbius molecules.[7] These same formulae were subsequently proved in Zimmerman's book[8]; this proof is, however, not a short one, making appeal, as it does, to the ideas of group theory and the use of trial solutions. In this note, therefore, we show how these results may be elegantly obtained, outside the immediate realms of HMO theory, by judicious exploitation of the theory of skew-circulant matrices.[10–12] The arguments called upon are entirely analogous to those previously invoked by one of us[13,14] to derive the orbital energies and HMO's of 'Hückel' annulenes from the theory of circulant matrices (e. g., ref. 13).

THE PROPERTIES OF CIRCULANT MATRICES

The circulant matrix

$$\begin{pmatrix} a_1 & a_n & a_3 & \cdots & a_n \\ a_n & a_1 & a_2 & \cdots & a_{n-1} \\ a_{n-1} & a_n & a_1 & \cdots & a_{n-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_2 & a_3 & a_4 & \cdots & a_1 \end{pmatrix}$$

has been shown[10–15] to have eigenvalues, $\{\lambda_k'\}$ $k = 1, 2, \ldots, n$, and eigenvectors, $\{V_k'\}$ $k = 1, 2, \ldots, n$, where

$$\lambda_k' = a_1 + a_2\,\omega_k + a_3\,\omega_k^2 + \ldots + a_n\,\omega_k^{n-1} \tag{1},$$

and

$$V_k' = \begin{pmatrix} 1 \\ \omega_k \\ \omega_k^2 \\ \cdot \\ \cdot \\ \cdot \\ \omega_k^{n-1} \end{pmatrix} \tag{2},$$

and ω_k is an n^{th} root of unity — i. e., one of the n roots of the scalar equation

$$\omega^n = 1 \tag{3}.$$

THE PROPERTIES OF SKEW-CIRCULANT MATRICES

We now show that the skew-circulant matrix B,

$$B = \begin{pmatrix} a_1 & a_2 & a_3 & \cdots & a_n \\ -a_n & a_1 & a_2 & \cdots & a_{n-1} \\ -a_{n-1} & -a_n & a_1 & \cdots & a_{n-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -a_2 & -a_3 & -a_4 & \cdots & a_1 \end{pmatrix}$$

has eigenvalues and eigenvectors formally given by equations (1) and (2), provided that ω_k in those equations is everywhere replaced by Θ_k, where Θ_k is an n^{th} root of minus one.

First consider the quantity

$$\lambda_k = a_1 + a_2\,\Theta_k + a_3\,\Theta_k^2 + \ldots + a_n\,\Theta_k^{n-1} \tag{4}$$

where Θ_k is one particular n^{th} root of minus one — i. e., one of the n roots of the scalar equation

$$\Theta^n = -1 \tag{5},$$

Equation (5) has solutions $\{\Theta_k\}$ $k = 1, 2, \ldots, n$, which are given by

$$\Theta_k = \cos[(2k+1)\pi/n] + i \sin[(2k+1)\pi/n] = \exp[(2k+1) i \pi/n] \tag{6}.$$

It will be clear from equations (4) and (5) that the following equations are true:

$$\begin{aligned}
\lambda_k &= a_1 + a_2 \Theta_k + a_3 \Theta_k^2 + \ldots + a_n \Theta_k^{n-1} \\
\Theta_k \lambda_k &= -a_n + a_1 \Theta_k + a_2 \Theta_k^2 + \ldots + a_{n-1} \Theta_k^{n-1} \\
\Theta_k^2 \lambda_k &= -a_{n-1} - a_n \Theta_k + a_1 \Theta_k^2 + \ldots + a_{n-2} \Theta_k^{n-1} \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\Theta_k^{n-1} \lambda_k &= -a_2 - a_3 \Theta_k - a_4 \Theta_k^2 - \ldots + a_1 \Theta_k^{n-1}
\end{aligned} \tag{7}$$

This set of equations implies the following matrix equation:

$$\begin{pmatrix}
a_1 & a_2 & a_3 & \cdots & a_n \\
-a_n & a_1 & a_2 & \cdots & a_{n-1} \\
-a_{n-1} & -a_n & a_1 & \cdots & a_{n-2} \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
-a_2 & -a_3 & -a_4 & \cdots & a_1
\end{pmatrix}
\begin{pmatrix} 1 \\ \Theta_k \\ \Theta_k^2 \\ \cdot \\ \cdot \\ \Theta_k^{n-1} \end{pmatrix}
= \lambda_k
\begin{pmatrix} 1 \\ \Theta_k \\ \Theta_k^2 \\ \cdot \\ \cdot \\ \Theta_k^{n-1} \end{pmatrix} \tag{8}$$

which, on the left-hand side, contains the skew-circulant matrix B. Hence, the vector*

$$V_k = \begin{pmatrix} 1 \\ \Theta_k \\ \Theta_k^2 \\ \cdot \\ \cdot \\ \Theta_k^{n-1} \end{pmatrix} \tag{9}$$

is an eigenvector of B, with eigenvalue λ_k given by equation (4). Since Θ_k is just one of the n roots (equation (6)) of equation (5), it follows that there will be a V_k (equation (9)) and a λ_k (equation (4)) corresponding to every distinct Θ_k, $k = 1, 2, \ldots, n$. $\{V_k\}$ $k = 1, 2, \ldots, n$ and $\{\lambda_k\}$ $k = 1, 2, \ldots, n$ are thus the complete set of eigenvectors and corresponding eigenvalues of B.

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* Or, (cf. Heilbronner's comment[1]), the appropriate real linear-combination of V_k and V_k^*, to give linear-combination-of-atomic-orbital (LCAO) molecular-orbitals (MO's) with real coefficients.

It should be noted that the set of eigenvectors, $\{V_k\}$, is the same for all skew-circulant matrices, but that the eigenvalues depend explicitly upon the elements that comprise any row of the particular skew-circulant matrix under consideration.

APPLICATION TO MÖBIUS ANNULENES

As may be seen from earlier work (e. g. refs. 1, 8, 16—19), a suitable adjacency-matrix for the cyclic graph C_n^M representing the carbon-atom connectivity of a Möbius $[n]$-annulene would be a skew-circulant matrix with first row $(0, 1, 0, \ldots, 0, -1)$ — that is, a matrix of the form**

$$A(C_n^M) = \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots & 0 & -1 \\ 1 & 0 & 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & 0 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ -1 & 0 & 0 & 0 & \cdots & 1 & 0 \end{pmatrix} \quad (10).$$

In the terminology of the matrix B, therefore, only a_2 $(= 1)$ and a_n $(= -1)$ are non-zero, and so, from equation (4),

$$\lambda_k = \Theta_k - \Theta_k^{n-1} \quad (11).$$

It follows from equation (5) that $\Theta_k^{n-1} = -\Theta_k^{-1}$, which allows us to write equation (11) as

$$\lambda_k = \Theta_k + \Theta_k^{-1}$$

whence, by equation (6), we obtain

$$\lambda_k = 2 \cos [(2k + 1)\, \pi/n] \quad (12).$$

The eigenvalue list for the matrix $A(C_n^M)$ is thus $\{\lambda_k\}$ $k = 1, 2, \ldots, n$. It should be observed that the eigenvalues are, of course, entirely real, since $A(C_n^M)$ is real-symmetric, even though this is not the case for the general skew-circulant matrix B.

Finally, since, in the HMO interpretation, orbital energies (ϵ_k^M) are measured in units of a resonance integral β' and with reference to a Coulomb integral α, namely,

$$\lambda_k = (\epsilon_k^M - \alpha)/\beta',$$

we may write equation (12) as

$$\epsilon_k^M = \alpha + 2\, \beta' \cos [(2k + 1)\, \pi/n] \quad (13).$$

The solution for the corresponding Hückel system takes the form

$$\epsilon_k^H = \alpha + 2\, \beta \cos (2k\, \pi/n) \quad (14).$$

** In its quantum-mechanical interpretation, equation (10) implies the choice of a basic set of atomic orbitals that has only a single $< \Phi_i \mid H \mid \Phi_j >$ — term negative. This choice is always possible for a Möbius ring.[1,8,16-19]

Writing β' in equation (13) and β in equation (14) allows for the fact that the dihedral angles (ω) between adjacent p-orbitals are different for a regular Möbius and a regular Hückel system — namely, π/n ($= \omega$) and zero, respectively, the resonance integrals being related by $\beta' = \beta \cos(\pi/n)$.

Comparison of the cosine term in equation (13), which may be expressed as $\cos(2k\pi/n + \pi/n)$, with that in equation (14) shows that the Möbius and the Hückel solutions for a given n are π/n »out of phase« with each other. In Frost and Musulin's mnemonic device[20] for representing the HMO energy-level spectrum of Hückel annulenes, the regular n-gon is oriented with one vertex »down«. The phase angle of π/n by which equations (13) and (14) differ corresponds in this context to a rotation of Frost and Musulin's polygon[20] through an angle of π/n — i. e., one half of the angle subtended by an edge of the polygon at its centre. That is why, in the corresponding mnemonic device introduced by Zimmerman[3,5-8] for Möbius systems, the regular polygon is oriented, in a circle of radius 2 β', with one edge »down«.

To complete the HMO interpretation, we recall[14] that the components of the eigenvector V_k of $A(C_n^M)$ (or appropriate linear-combinations of V_k and V_k^* if real coefficients are required[1,8,16]) are the weighting coefficients of the individual basis atomic-orbitals, $\{\Phi_\mu\}_{\mu=1,2,\ldots,n}$, of the k^{th} linear-combination-of-atomic-orbitals Hückel MO, Ψ_k, for the Möbius $[n]$-annulene — i. e. (cf. refs. 1, 8):

$$\Psi_k = n^{-1/2} \sum_{\mu=1}^{n} (\Theta_k)^{\mu-1} \Phi_\mu = n^{-1/2} \sum_{\mu=1}^{n} \{\exp[(2k+1)(\mu-1)\,i\,\pi/n]\}\,\Phi_\mu \qquad (15),$$

the last step being via equation (6).

In the course of discussion of this paper at the Symposium in Dubrovnik, Professor D. J. Klein kindly pointed out[21] to the author who read the paper at the Symposium (R. B. M.) that the solution to the Möbius/Hückel matrix-problem may also be effected (a) by use of double-group representation[7] and (b) by application of a suitable (diagonal) unitary-transformation to yield an Hermitian (though not real) circulant-matrix.[21] Professor Klein also made the intriguing observation[21] that the eigenvalue problem pertaining to the Möbius/Hückel type of matrix may be generalised in other ways: one generalisation is to a matrix in which the two elements that, in the conversion of a 'Hückel' matrix into a 'Möbius' one, are changed from $+1$ to -1 are replaced by $e^{i\Phi}$ and $e^{-i\Phi}$ (Φ being real). (A 'Hückel' matrix therefore corresponds to $\Phi = 2k\pi$, k an integer, while the 'Möbius' matrix is reproduced when $\Phi = (2k+1)\pi$). The eigenvalue solution to this matrix may then be obtained[21] via method (b), above, and constitutes a simple generalisation of the Frost-Musulin[20] 'shadow diagram'[21]: their polygon is simply rotated by Φ/n. A second generalisation is in terms of a Pariser-Parr-Pople type of model that includes electron-electron interaction[22]; in this case, simple, elegant solutions do not seem to be known[21], though some general properties of the ground-state eigen-solution have recently been established.[23]

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SAŽETAK

Dokaz formula za molekularne orbitale i energijske razine Möbiusovih anulena zasnovan na teoriji specijalnih cikličkih matrica

A. C. Day, R. B. Mallion i M. J. Rigby

Izvedene su formule za molekularne orbitale i energijske razine, koje se javljaju u okvirima Hückelove MO teorije, i to za Möbiusove anulene, s pomoću teorije specijalnih cikličkih matrica.