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Correlation between Fourier series expansion and Hückel orbital theory

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Abstract The Fourier series can be used to describe periodic phenomena such as the one-dimensional crystal wave function. By the trigonometric treatements in Hückel theory it is shown that Hückel theory is a special case of Fourier series theory. Thus, the conjugated π system is in fact a periodic system. Therefore, it can be explained why such a simple theorem as Hückel theory can be so powerful in organic chemistry. Although it only considers the immediate neighboring interactions, it implicitly takes account of the periodicity in the complete picture where all the interactions are considered. Furthermore, the success of the trigonometric methods in Hückel theory is not accidental, as it based on the fact that Hückel theory is a specific example of the more general method of Fourier series expansion. It is also important for education purposes to expand a specific approach such as Hückel theory into a more general method such as Fourier series expansion.

Keywords Periodicity · Conjugated π system · Crystal wave function · Symmetric and anti-symmetric function · Chemical education

1 Introduction

Hückel theory [1,2] plays an important role in theoretical organic chemistry. The concepts involved in Hückel theory have been connected with valence bond theories [3]

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and configuration interaction [4,5]. Several different methods, some involving trigonometric functions [6–8], have been used to simplify the mathematical treatments in Hückel theory and in particular solve wave-functions [9]. In this paper we will show that the trigonometric methods used in Hückel theory [10,11] can be incorporated into the more general principles of Fourier series expansion which is predominantly used in many fields to describe period phenomena. The connection with energy band theory for crystals is also considered here. The connection between Hückel theory and Fourier series theory has not been pointed out explicitly previously to our knowledge.

2 General solutions

The method of Fourier series is a general method that is applicable to period phenomena. Examples include the electron density in a crystal [12] and a one-dimensional crystal wave function with periodicity a as shown in Eq. 1 [13].

$$\Psi(x) = \sum_{j=1}^{N} k_j \frac{1}{\sqrt{L}} e^{i\left(j\frac{2\pi}{a}x\right)} \tag{1}$$

where L is the cell length in the crystal containing N atoms. k_j is a constant. In the linear combination of atomic orbitals to crystal orbital (LCAO-CO) or tight-bonding approximation, the symmetry adapted [15,16] crystal orbital can be represented in Fourier series form [14,17] where every atom contributes a p_y orbital. The molecular orbital of a conjugated system with N atoms is a linear combination of atomic orbitals as shown in Eq. 2a.

$$\psi(\mathbf{R}) = \frac{1}{\sqrt{\sum_{j=1}^{N} c_j^2}} \sum_{j=1}^{N} c_j \phi_{p_y}(\mathbf{R} - j\mathbf{a}) = \frac{1}{\sqrt{\sum_{j=1}^{N} c_j^2}} \sum_{j=1}^{N} c_j \phi_{p_y}\left(\mathbf{r}_j\right) \tag{2a}$$

c_j is the j'th expanding coefficient. $\phi_{p_y}(\mathbf{r}_j)$ is the atomic orbital located on atom j of the coordinate system. This equation can be simplified from three dimensions to one to give Eq. 2b

$$\Psi(x) = \frac{1}{\sqrt{\sum_{j=1}^{N} c_j^2}} \sum_{j=1}^{N} c_j \phi_{p_y}(x - ja) \tag{2b}$$

Figure 1 shows a one-dimensional crystal with a periodicity represented by vector **a**. The length of **a** is denoted by a in Eq. 2b. The conjugated system can also be considered as a limited periodic system with the value of j ranging from 1 to N.

We can equate the one-dimensional crystal wave function of periodicity a as shown in Eq. 1 with the molecular orbital of an N-atom conjugated system as shown in Eq. 2b and demonstrate that they represent mutually inverse Fourier series by proving Eqs. 3a and 3b.

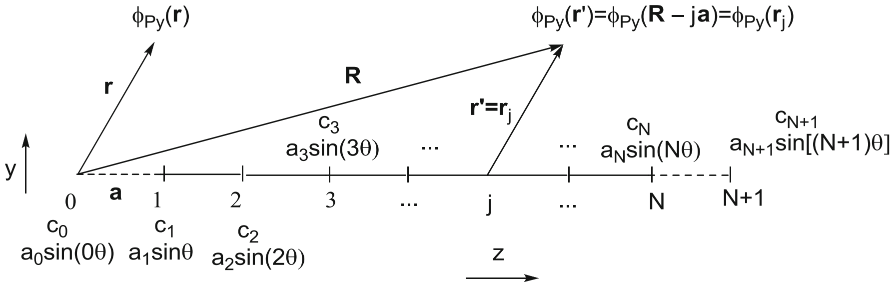


Fig. 1 One dimensional crystal with translation vector **a**. Vectors are indicated in *bold*. The atoms are located at the points labeled by integers. The periodic vector **a** connects adjacent atoms. The atomic wave-function $\phi_{py}(\mathbf{r} - j\mathbf{a})$ is translated from the function $\phi_{py}(\mathbf{r})$ at atom 0. The trigonometric functions labeled near the atom sites are the coefficients c_j in the Fourier series expansion. The derivation of these coefficients is given in the main text

$$k_j = \phi_{p_y}(x - ja) \tag{3a}$$

$$c_j = e^{i\left(j\frac{2\pi}{a}x\right)} \tag{3b}$$

In fact taking into account the concept of symmetry adapted orbitals, Eq. 1 can be written as

$$\Psi(x) = \sum_{j=1}^{N} e^{i(j-1)\frac{2\pi}{N}} \phi_{p_{yt}}(\mathbf{r}_j)$$

for conjugated systems [16].

2.1 *Proof* 1: Eqs. 1 and 2b are mutually inverse Fourier series

Here it is demonstrated that Eqs. 1 and 2b represent mutually inverse Fourier series. Equations 4–7 are the secular equations of Hückel theory.

$$c_1(\alpha - E) + c_2\beta = 0 \tag{4}$$

$$c_1\beta + c_2(\alpha - E) + c_3\beta = 0 \tag{5}$$

$$\ldots$$

$$c_{j-1}\beta + c_j(\alpha - E) + c_{j+1}\beta = 0 \tag{6}$$

$$\ldots$$

$$c_{N-1}(\alpha - E) + c_N\beta = 0 \tag{7}$$

where α is the Coulomb integral, β is the exchange integral for adjacent atoms. If

$$c_j = e^{i(j\theta)} = e^{i\left(j\frac{2\pi}{a}x\right)}; \quad \text{where } \theta = \frac{2\pi}{a}x \tag{8}$$

then Eq. 9 is satisfied from Eq. 6.

$$e^{i(j\theta)}\left[\beta e^{-i\theta}+(\alpha-E)+\beta e^{i\theta}\right]=0 \tag{9}$$

From Eq. 9 we can obtain Eq. 10 which correlates the energy E with θ.

$$-y=\frac{\alpha-E}{\beta}=-\left[e^{i\theta}+e^{-i\theta}\right]=-2\cos\theta \tag{10}$$

If Eq. 8 is the solution of the secular equations, then Eq. 11 is also valid.

$$c_j=e^{-j\theta i} \tag{11}$$

$$e^{-i(j\theta)}\left[\beta e^{-i\theta}+(\alpha-E)+\beta e^{i\theta}\right]=0 \tag{12}$$

Equations 8 and 11 give two specific solutions to the secular equations and the general solution should be Eq. 13 which can be proved from Eq. 14.

$$c_j=Ae^{i(j\theta)}+Be^{-i(j\theta)}=(A+B)\cos(j\theta)+i(A-B)\sin(j\theta)=c\sin\left(j\theta+\omega\right)$$
$$\text{where } c=\frac{1}{\sqrt{(A+B)^2+(A-B)^2}} \quad \text{and} \quad \sin\omega=(A+B)c \tag{13}$$

A and B in Eq. 13 represent arbitrary numbers for the general solution but they can be determined from the appropriate boundary conditions for specific cases.

$$Ae^{i(j\theta)}\left[\beta e^{-i\theta}+(\alpha-E)+\beta e^{i\theta}\right]+Be^{-i(j\theta)}\left[\beta e^{-i\theta}+(\alpha-E)+\beta e^{i\theta}\right]=0 \tag{14}$$

The Laplace transformation is a well-known method which can be used to solve differential equations [18]. Boundary conditions are particularly important in such calculations and those for a conjugated straight chain polyene with N atoms in the secular equations of Hückel theory are given in Eq. 15.

$$c_0=0; \quad \text{and} \quad c_{N+1}=0 \tag{15}$$

By normalizing the wave function and inserting the boundary conditions given in Eq. 15 into Eq. 13 we can obtain the solutions for the secular equations of Hückel theory which will provide values of θ and the constants A and B (or c and ω). From c_0 = 0 which terminates the wave function from the left, we obtain that ω = 0 via Eq. 13 for the conjugated straight chain polyene and from c_{N+1} = 0 which terminates the wave function from the right, we obtain Eq. 16.

$$\theta=\frac{m\pi}{N+1}; \qquad \text{m}=1,2,\ldots,N \tag{16}$$

An empty orbital is obtained for m = 0. When the value of m is greater than N, then m is taken as mod(m, N) since the results for the wave-function and its energy will repeat from those for m = 0, 1, …, N. So, only N independent orbitals are obtained. The above results reduce Eqs. 1 and 2b to Eq. 17.

$$\begin{aligned}\psi(\mathbf{R}) &= \sqrt{\frac{2}{\text{N+1}}}\left[\sin\theta\cdot\phi_{p_y}(\mathbf{R}-\mathbf{a})+\sin 2\theta\cdot\phi_{p_y}(\mathbf{R}-2\mathbf{a})\right.\\ &\quad\left.+\cdots+\sin N\theta\cdot\phi_{p_y}(\mathbf{R}-N\mathbf{a})\right]\\ &= \sqrt{\frac{2}{\text{N+1}}}\sum_{j=1}^{N}\left[\sin j\theta\cdot\phi_{p_y}(\mathbf{R}-j\mathbf{a})\right]\end{aligned}\tag{17}$$

The coefficients in Eq. 17 where $c_j = a_j \sin(j\theta)$ are illustrated in Fig. 1 where all the a_j are equal to a_1. A derivation of the normalizing constants a_1 in Eq. 18 is given in "Appendix 2".

$$a_1 = \sqrt{\frac{2}{N+1}}\tag{18}$$

Now let us consider cyclic conjugated polyenes. Only the first and the last equations (Eqs. 4 and 7) in the secular equations of Hückel theory will be different from those which were used for the straight chain polyenes. The boundary conditions for cyclic conjugated polyenes are given in Eq. 19.

$$c_0 = c_N\tag{19}$$

By inserting Eq. 19 into Eq. 13 we obtain Eq. 20.

$$c_N = c\sin(N\theta+\omega) = c\sin\omega = c_0\tag{20}$$

From Eq. 20, we obtain

$$N\theta+\omega = \omega+2m\pi;\quad \theta = \frac{2m\pi}{N};\quad m = 0, 1, 2, \ldots, N-1\tag{21}$$

Equation 21 can also be obtained from other methods such as cyclic symmetry operations [15] as shown in "Appendix 1".

Other methods leading to Eqs. 16 and 21 are given in "Appendix 1". By inserting Eq. 21 into Eq. 10, the expression of the orbital energy for a cyclic conjugated polyene is obtained (Eq. 22).

$$E = \alpha+2\beta\cos\theta = \alpha+2\beta\cos\frac{2m\pi}{N}\tag{22}$$

A diagrammetric representation of orbital energy for a cyclic conjugated polyene is presented in Fig. 2. Together with Eqs. 10, 16, 21 and A1, it provides a way to calculate

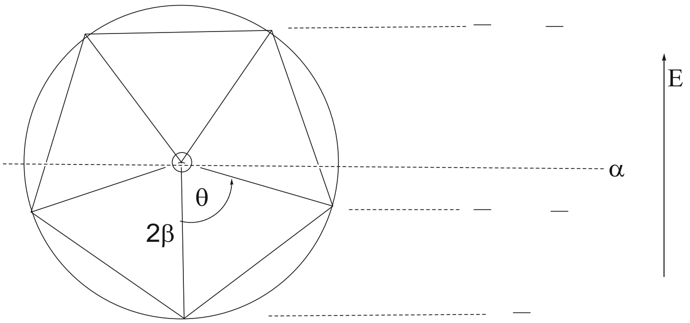


Fig. 2 Pictorial representation of the orbital energy for cyclic conjugated polyene using Eq. 21 with a regular polygonal of N = 5 inside a circle of appropriate radius 2β, noting that $E = \alpha + 2\beta \cos\theta$

cos[mπ/(N + 1)] or cos(2mπ/N). Other ways to calculate cos[mπ/(N + 1)] which are relevant for obtaining orbital energy are given in "Appendix 4".

Similarly to Eq. 16, Eq. 21 signifies that there are N molecular orbitals in a cyclic conjugated polyene of N atoms. In the example shown in Fig. 2, N = 5. The trigonometric identity Eq. 23 can be applied to Eq. 20 to give Eq. 24.

$$\sin\omega = \sin(\pi - \omega) \tag{23}$$

$$c_N = c\sin\omega = c_0 = c\sin(\pi - \omega) \tag{24}$$

This leads to Eqs. 25 and 26 which are derived in "Appendix 5".

$$\sin(j\theta + \omega) = \sin[j\theta + (\pi - \omega)] \tag{25}$$

$$c_{N+j} = c\sin(\pi - \omega + j\theta) = c\sin(j\theta + \omega) = c_j \tag{26}$$

When j = 0, Eq. 25 becomes equivalent to Eq. 23. In order to insure that Eq. 25 is true for any value of j, Eq. 27 must be satisfied.

$$j\theta + \omega = j\theta + (\pi - \omega)\,; \qquad \omega = \frac{\pi}{2} \tag{27}$$

Hence in a cyclic conjugated system

$$c_j = c\sin\left(j\theta + \frac{\pi}{2}\right) = c\cos j\theta = c\cos\frac{2jm\pi}{N} \tag{28}$$

Therefore using Eq. 16, we have obtained Eq. 17 from Eqs. 13 and 15 for the N molecular orbitals of an open chain conjugated polyene and Eq. 28 from Eqs. 13 and 25 for a cyclic conjugated polyene. The energies of the orbitals can be obtained from Eq. 10 via Eq. 16 or 21. It is thus clear that Eqs. 3a and 3b are valid since the necessary values of θ have been obtained. Therefore, Eqs. 1 and 2b form an inverse Fourier series relationship. The coefficients c_j for the open chain polyene of N atoms have been calculated from Eqs. 13 and 17 where $\omega = 0$ and the values of θ are taken from

Eq. 16. The coefficients of c_j are shown in Fig. 1. Another form of Eq. 2b is shown as Eq. 29.

$$\begin{aligned}\Psi_k(x) &= c_1\phi_{p_y}(x-a) + c_2\phi_{p_y}(x-2a) + \cdots + c_N\phi_{p_y}(x-Na)\\ &= \sum_{j=1}^{N} c_j\phi_{p_y}(x-ja)\\ &= \sum_{j=1}^{N} a_j\sin(j\theta)\cdot\phi_{p_y}(x-ja) + \sum_{j=1}^{N} b_j\cos(j\theta)\cdot\phi_{p_y}(x-ja)\end{aligned} \quad (29)$$

With Eq. 6 and the boundary conditions given in Eq. 15 for straight chain polyenes, we can prove that all a_j are equal and all b_j are equal to 0 for $j=1$ to N, and that the coefficients which are shown in Fig. 1 can be calculated.

3 General solutions for a conjugated straight chain polyene

3.1 *Proof 2:* proof of Eq. 29 where $b_j = 0$ for a conjugated straight chain polyene

Here we show that Eq. 29 is another form of Eq. 2b for a conjugated straight chain polyene. From Eqs. 6 and 10, we obtain Eq. 30 as shown below. From Eq. 6 we obtain

$$c_{j-1} + c_j\frac{\alpha - E}{\beta} + c_{j+1} = 0$$

Substituting Eq. 10, where $y = 2\cos\theta$, we obtain

$$c_{j-1} + c_{j+1} = c_j\frac{E-\alpha}{\beta} = yc_j = 2c_j\cos\theta$$

or

$$c_{j-1} + c_{j+1} = 2\cos\theta\cdot c_j \quad (30)$$

If a central atom j in a conjugated system is bonded to a third atom x, then Eq. 30 can be expanded to Eq. 31 in which the sum of the coefficients of the atoms connected to the central atom will equal the coefficient of the central atom times $2\cos\theta$.

$$\mathrm{c}_{j-1} + \mathrm{c}_{j+1} + \mathrm{c}_x = 2\mathrm{c}_j\cos\theta \quad (31)$$

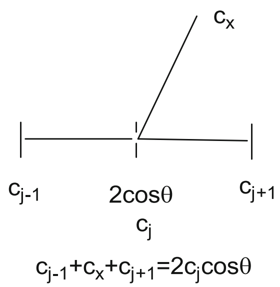
and this is illustrated in Fig. 3.

In the example shown in Fig. 3, Eq. 6 can be expanded to give

$$c_{j-1}\beta + c_x\beta + c_j(\alpha - E) + c_{j+1}\beta = 0 \quad (32)$$

$$c_{j-1} + c_x + c_{j+1} = c_j\frac{E-\alpha}{\beta} = 2c_j\cos\theta \quad (33)$$

Fig. 3 A graphical representation of 3 carbon atoms attached to a central carbon atom j



Equations 30 and 33 can be used to calculate all the coefficients in Eq. 29 by trignometrical identity [19]. i. e. setting j = 1, given that $c_0 = 0$ and $c_1 = a_1 \sin\theta$, c_2 can be obtained from Eq. 34.

$$0 + c_2 = 2\cos\theta \cdot a_1 \sin\theta = a_1 \sin(2\theta) \tag{34}$$

In general terms, then we can obtain all coefficients c_{j+1} from Eq. 35 which is derived from Eq. 30.

$$\begin{aligned} &a_1 \sin[(j-1)\theta] + c_{j+1} = 2\cos\theta \cdot a_1 \sin(j\theta) = a_1 \sin(\theta + j\theta) - a_1 \sin(\theta - j\theta) \\ &c_{j+1} = a_1 \sin[(j+1)\theta] \end{aligned} \tag{35}$$

The results obtained from Eq. 35 are shown in Fig. 1. Using the boundary condition $c_{N+1} = 0$, θ can be determined in the same manner that Eq. 16 is obtained. Similarly, an empty function is given when m = 0. Thus, all the b_j should be 0.

There are always the same number of symmetry and anti-symmetry orbitals with respect to mirror or two fold rotation symmetry operations in Hückel theory. Similarly there are odd and even expansions of Fourier series which are expressed in terms of sines and cosines, respectively. This property can be used to simplify the treatment further as discussed in the following sections. More examples will be provided in "Appendix 3".

4 Symmetric and anti-symmetric wave functions for conjugated straight chain polyenes when N is even

The coefficients of the symmetric and the anti-symmetric wave function can be calculated from the centre, marked as 0, in Fig. 4 when N is even. Thus, the angle in the coefficients for the two atoms making up the central bond is $\theta/2$. From Eq. 6 we can obtain the coefficients for both the odd and even functions. The coefficients obtained from Eqs. 36 and 37 are shown in Fig. 4. When N is odd the same derivation applies and the results are shown in Fig. 5.

$$-\sin\frac{\theta}{2} + c_{3/2} = 2\cos\theta \cdot \sin\frac{\theta}{2} = \sin\left(\theta + \frac{\theta}{2}\right) - \sin\left(\theta - \frac{\theta}{2}\right)$$

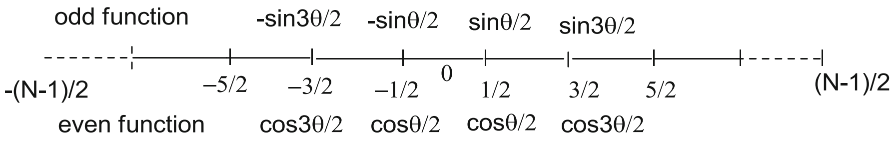


Fig. 4 A representation of a conjugated straight chain polyene where N is even. The coefficients for the odd and even functions are also shown with the angle form of $\pm[(1/2)+0]\theta, \pm[(1/2)+1]\theta, \pm[(1/2)+2]\theta, \pm[(1/2)+3]\theta, \ldots, \pm[(1/2)+j]\theta, \ldots \pm\{(1/2)+[(N/2)-1]\}\theta$

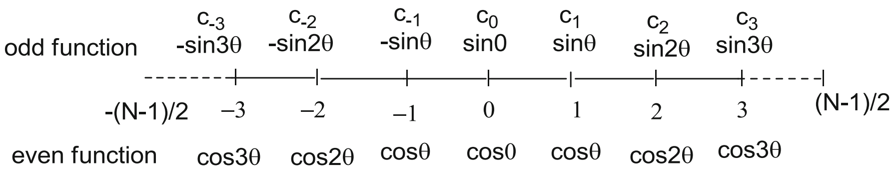


Fig. 5 A representation of a conjugated straight chain polyene where N is odd. The coefficients for the odd and even function are derived from Eq. 30 and shown with the angle form of $0 = [N-(N-0)/2]\theta, \pm 1\theta = \pm\{[N-(N-2)]/2\}\theta; \pm 2\theta = \pm\{[N-(N-4)]/2\}\theta; \ldots; \pm j\theta = \pm\{[N-(N-2j)]/2\}\theta; \ldots; \pm[(N-5)/2]\theta = \pm\theta\{N-[N-(N-5)]\}/2; \pm[(N-3)/2]\theta = \pm\theta\{N-[N-(N-3)]\}/2; \pm[(N-1)/2]\theta = \pm\theta\{N-[N-(N-1)]\}/2$. Notice that $N-3$ in $[N-(N-3)]$ or $N-1$ in $[N-(N-1)]$ is an even number accounted for $2j$

$$= \sin\left(\frac{3\theta}{2}\right) - \sin\left(\frac{\theta}{2}\right); \quad c_{3/2} = \sin\left(\frac{3\theta}{2}\right) \tag{36}$$

$$\cos\frac{2j-3}{2}\theta + c_{(j+1)/2} = 2\cos\theta \cdot \cos\frac{2j-1}{2}\theta = \cos\left(\theta + \frac{2j-1}{2}\theta\right)$$
$$+\cos\left(\theta - \frac{2j-1}{2}\theta\right) = \cos\left(\frac{2j+1}{2}\theta\right) + \cos\left(\frac{2j-3}{2}\theta\right);$$
$$c_{(j+1)/2} = \cos\left(\frac{2j+1}{2}\theta\right) \tag{37}$$

The boundary conditions are represented by Eqs. 38 and 39 for the even and odd functions, respectively.

$$c_{\frac{N+1}{2}} = \cos\left(\frac{N+1}{2}\theta\right) = 0; \quad \theta = \frac{2m+1}{N+1}\pi; \quad m = 0, 1, 2, \ldots, < \frac{N}{2} \tag{38}$$

$$c_{\frac{N+1}{2}} = \sin\left(\frac{N+1}{2}\theta\right) = 0; \quad \theta = \frac{2m\pi}{N+1}; \quad m = 1, 2, \ldots, \frac{N}{2} \tag{39}$$

Equations 38 and 39 give N molecular orbitals.

5 Symmetric and anti-symmetric wave functions for conjugated straight chain polyenes when N is odd

The boundary conditions for the even and odd functions respectively are given in Eqs. 40 and 41 when N is odd.

$$c_{\frac{N+1}{2}} = \cos\left(\frac{N+1}{2}\theta\right) = 0; \quad \theta = \frac{2m+1}{N+1}\pi; \quad m = 0, 1, 2, \ldots, \frac{N-1}{2} \tag{40}$$

$$c_{\frac{N+1}{2}} = \sin\left(\frac{N+1}{2}\theta\right) = 0; \quad \theta = \frac{2m\pi}{N+1}; \quad m = 1, 2, \ldots, \frac{N-1}{2} \tag{41}$$

The coefficients of the symmetric and the anti-symmetric wave function can be calculated from the θ valuues of Eqs. 40 and 41. There are N molecular orbitals and the coeffecients are shown in Fig. 5.

6 Conclusions

The simple Hückel theory is useful in theoretical organic chemistry. The trigonometric basis of this theory is a very powerful mathematical method. However, the trigonometric treatment seems an isolated case not applicable to other systems. In this paper, however, a significant correlation between Fourier series expansion and Hückel orbital theory is shown by the trigonometric treatments. The correlation is interesting since the form of Hückel orbital theory looks very different from that of Fourier series expansion. The universal success of Huckel theory in explaining the properties of conjugated organic molecules can thus be attributed to its sound theoretical basis which is related to Fourier series expansion, a generally accepted theory in many fields for periodic phenomena. In fact, an active research strategy is often obtained by connecting different concepts or methodologies [20–23].

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Appendices

The appendices that are included here provide background information for chemists who are not familiar with the mathematics involved. Different methods are provided to show that the success of Hückel theory is not accidental. Some of the derivations presented here are original; others are based on the given references. Equations not in the main text but introduced here are denoted with an A prefix.

Appendix 1: Other methods of obtaining Eqs. 16 and 21

Method 1

The secular equations for a conjugated straight chain polyene is given by Eq. A1.

$$g_n(y) = \begin{vmatrix} y & -1 & 0 & \dots & 0 \\ -1 & y & -1 & \dots & 0 \\ 0 & \dots & \dots & \dots & 0 \\ \dots & \dots & -1 & y & -1 \\ 0 & \dots & 0 & -1 & y \end{vmatrix} = 0 \tag{A1}$$

From Eq. A1, Eq. A2 can be obtained.

$$g_n(y) = yg_{n-1}(y) - g_{n-2}(y) = 0 \tag{A2}$$

From Eqs. A1 and A2, Eqs. A3–A8 are obtained.

$$g_0(y) = 1 \tag{A3}$$

$$g_1(y) = y \tag{A4}$$

$$g_2(y) = y^2 - 1 \tag{A5}$$

$$g_3(y) = y^3 - 2y \tag{A6}$$

$$\begin{aligned} g_4(y) &= y^4 - 3y^2 + 1 = (-1)^0 \frac{(4-0)!}{0!\,(4-2\cdot 0)!} y^{4-2\cdot 0} \\ &\quad + (-1)^1 \frac{(4-1)!}{1!\,(4-2\cdot 1)!} y^{4-2\cdot 1} + (-1)^2 \frac{(4-2)!}{2!\,(4-2\cdot 2)!} y^{4-2\cdot 2} \end{aligned} \tag{A7}$$

$$\dots$$

$$\begin{aligned} g_N(y) &= (-1)^0 \frac{(N-0)!}{0!\,(N-2\cdot 0)!} y^{N-2\cdot 0} + (-1)^1 \frac{(N-1)!}{1!\,(N-2\cdot 1)!} y^{N-2\cdot 1} \\ &\quad + \dots + (-1)^j \frac{(N-j)!}{j!\,(N-2\cdot j)!} y^{N-2\cdot j} = \sum_j (-1)^j \frac{(N-j)!}{j!\,(N-2\cdot j)!} y^{N-2\cdot j} \end{aligned} \tag{A8}$$

When N is even, $j \leq N/2$ for Eq. A8. When N is odd, $j \leq (N-1)/2$. We can obtain a general formulae for $g_n(y)$ as follows. Starting from the identity Eq. A9 where $a = yz$ and $b = z^2$.

$$\begin{aligned} \sum_{N=0}^{\infty} \sum_{j=0}^{N} (a-b)^N &= \sum_{N=0}^{\infty} \sum_{j=0}^{N} (yz - z^2)^N = \sum_{N=0}^{\infty} \sum_{j=0}^{N} (-1)^j C_N^j (yz)^{N-j} z^{2j} \\ &= \sum_{N=0}^{\infty} \sum_{j=0}^{j \leq N/2} (-1)^j C_{N-j}^j (yz)^{N-j-j} z^{2j} \\ &= \sum_{N=0}^{\infty} \left[\left(\sum_{j=0}^{j \leq N/2} (-1)^j C_{N-j}^j y^{N-2j} \right) z^N \right] \end{aligned} \tag{A9}$$

In Eq. A9, all terms with the same power of z are combined. Since

$$\sum_{N=0}^{\infty}(yz-z^2)^N = 1+(yz-z^2)+(yz-z^2)^2+\cdots+(yz-z^2)^N = \frac{1}{1-(yz-z^2)} \tag{A10}$$

$yz-z^2<1$. By comparing the coefficients of z^N in Eq. A9 with those in Eq. A8, it can be seen that $g_n(y)$ represents the coefficient of z^N in Eq. A9. Thus, Eq. A11 can be readily obtained from Eqs. A8 to A10.

$$\begin{aligned}\sum_N g_N(y)z^N &= \sum_N\sum_{j=0}^{N/2}(-1)^j\,\frac{(N-j)!}{j!\,(N-2\cdot j)!}y^{N-2\cdot j}z^N \\ &= \sum_N\sum_{j=0}^{N/2}(-1)^j\,C_{N-j}^{j}y^{N-2\cdot j}z^N = \left(1-yz+z^2\right)^{-1}\end{aligned} \tag{A11}$$

Using the definition specified in Eq. 10 we obtain Eq. A12.

$$\begin{aligned}\left(1-yz+z^2\right)^{-1} &= (1-2z\cos\theta+z^2)^{-1} = [1-z\left(e^{i\theta}+e^{-i\theta}\right)+ze^{i\theta}ze^{-i\theta}]^{-1} \\ &= \left[\left(1-ze^{-i\theta}\right)-ze^{i\theta}\left(1-ze^{-i\theta}\right)\right]^{-1} = \frac{1}{(1-ze^{i\theta})(1-ze^{-i\theta})} \\ &= \frac{\left(e^{i\theta}-e^{-i\theta}\right)-ze^{i\theta}e^{-i\theta}+ze^{i\theta}e^{-i\theta}}{2i\sin\theta(1-ze^{i\theta})(1-ze^{-i\theta})} \\ &= \frac{e^{i\theta}\left(1-ze^{-i\theta}\right)-e^{-i\theta}(1-ze^{i\theta})}{2i\sin\theta(1-ze^{i\theta})(1-ze^{-i\theta})} \\ &= (2i\sin\theta)^{-1}\left(\frac{e^{i\theta}}{1-ze^{i\theta}}-\frac{e^{-i\theta}}{1-ze^{-i\theta}}\right) \\ &= (2i\sin\theta)^{-1}\left[e^{i\theta}\left(1+ze^{i\theta}+\cdots+z^Ne^{iN\theta}\right)\right. \\ &\quad \left.-e^{-i\theta}\left(1+ze^{-i\theta}+\cdots+z^Ne^{-iN\theta}\right)\right] \\ &= (2i\sin\theta)^{-1}\sum_N z^N\left(e^{i(N+1)\theta}-e^{-i(N+1)\theta}\right) \\ &= \sum_N\frac{\sin(N+1)\theta}{\sin\theta}z^N\end{aligned} \tag{A12}$$

Thus, Eq. A13 is obtained from Eq. A11 via Eq. A12.

$$g_N(y) = \frac{\sin(N+1)\theta}{\sin\theta} \tag{A13}$$

Equation 16 is thus obtained from Eq. A13 by the requirement of Eq. A1. The polynomial for the secular equations pertaining to a cyclic conjugated polyene is given as Eq. A14.

$$P_n(y) = yg_{n-1}(y) - 2g_{n-2}(y) - 2 = g_n(y) - g_{n-2}(y) - 2 \tag{A14}$$

Equation A15 is obtained by inserting Eq. A13 into Eq. A14.

$$P_n(y) = \frac{1}{sin\theta}\left[\sin(N+1)\theta - \sin(N-1)\theta\right] - 2 = 2\left(\cos N\theta - 1\right) \tag{A15}$$

Equation 21 can thus be obtained from Eq. A15.

Method 2

From mathematical induction it is easy to prove

$$G_N = \begin{vmatrix} a+b & ab & 0 & \dots & 0 \\ 1 & a+b & ab & \dots & 0 \\ 0 & \dots & \dots & \dots & 0 \\ \dots & \dots & 1 & a+b & ab \\ 0 & \dots & 0 & 1 & a+b \end{vmatrix} = \frac{a^{N+1} - b^{N+1}}{a-b} \tag{A16}$$

The validity of the relationship can be easily seen for small values of N such as 2 or 3. Using Eq. A2 we can prove that Eq. A17 is valid. i.e. if the relationship is valid for order N, then expanding the determinant for order N + 1, we obtain

$$\begin{aligned} \mathrm{G}_{N+1} &= (a+b)\mathrm{G}_N - ab\mathrm{G}_{N-1} = (a+b)\frac{a^{N+1} - b^{N+1}}{a-b} - ab\frac{a^N - b^N}{a-b} \\ &= \frac{a^{(N+1)+1} - b^{(N+1)+1}}{a-b} \end{aligned} \tag{A17}$$

Let

$$a = -e^{i\theta}; \quad \text{and} \quad b = -e^{-i\theta} \tag{A18}$$

then

$$a + b = -2\cos\theta; \quad \text{and} \quad ab = 1 \tag{A19}$$

From Eq. A1 we have

$$g_N(y) = \begin{vmatrix} y & -1 & 0 & \dots & 0 \\ -1 & y & -1 & \dots & 0 \\ 0 & \dots & \dots & \dots & 0 \\ \dots & \dots & -1 & y & -1 \\ 0 & \dots & 0 & -1 & y \end{vmatrix}$$

$$= (-1)^N \begin{vmatrix} -2\cos\theta & 1 & 0 & \dots & 0 \\ 1 & -2\cos\theta & 1 & \dots & 0 \\ 0 & \dots & \dots & \dots & 0 \\ \dots & \dots & 1 & -2\cos\theta & 1 \\ 0 & \dots & 0 & 1 & -2\cos\theta \end{vmatrix}$$

$$= (-1)^N \frac{(-1)^{N+1}[e^{i(N+1)\theta} - e^{-i(N+1)\theta}]}{-(e^{i\theta} - e^{-i\theta})} = \frac{2i\,\sin(N+1)\theta}{2i\,\sin\theta} \tag{A20}$$

The result obtained from Eq. A20 is the same as that from Eq. A13.

Method 3: The proof of Eq. 21 following ref. [15]

Equation 2a for a system with cyclic symmetry can be written as

$$\psi = \sum_{j=1}^{N} c_j \phi_{p_y}\left(\mathbf{r}_j\right) = \sum_{j=1}^{N} c_{j+n} \phi_{p_y}\left(\mathbf{r}_{j+n}\right);\ \text{modulo } N \tag{A21}$$

The cyclic group C_N with elements

$$\{C_N^n;\, n = 1, 2, \dots, N\} \tag{A22}$$

has only one-dimensional irreducible representations with the characters

$$\chi(C_N^n) = e^{2\pi imn/N} \tag{A23}$$

By definition

$$C_N^n \phi_{p_y}\left(\mathbf{r}_j\right) = \phi_{p_y}\left(\mathbf{r}_{j+n}\right);\ \text{modulo } N \tag{A24}$$

and

$$C_N^n \psi = e^{2\pi imn/N} \psi \tag{A25}$$

Since

$$e^{2\pi imn/N} \psi = e^{2\pi imn/N} \sum_{j=1}^{N} c_j \phi_{p_y}\left(\mathbf{r}_j\right) = e^{2\pi imn/N} \sum_{j=1}^{N} c_{j+n} \phi_{p_y}\left(\mathbf{r}_{j+n}\right) \tag{A26}$$

The C_N^n operator in Eq. A25 will affect the $\phi_{p_y}\left(\mathbf{r}_j\right)$ function in Eq. A21 but not the constants c_j. Thus from Eq. A25 we obtain Eq. A27.

$$C_N^n \psi = \sum_{j=1}^{N} c_j C_N^n \phi_{p_y}\left(\mathbf{r}_j\right) = \sum_{j=1}^{N} c_j \phi_{p_y}\left(\mathbf{r}_{j+n}\right) \tag{A27}$$

From Eqs. A27, A25, and A26 we obtain Eq. A28.

$$\sum_{j=1}^{N} c_j \phi_{p_y}\left(\mathbf{r}_{j+n}\right) = e^{2\pi imn/N} \sum_{j=1}^{N} c_{j+n} \phi_{p_y}\left(\mathbf{r}_{j+n}\right) \tag{A28}$$

Equation A28 implies that

$$\begin{aligned} c_j &= e^{2\pi imn/N} c_{j+n}; \text{ or} \\ e^{-2\pi imn/N} c_j &= c_{j+n} \end{aligned} \tag{A29}$$

Using Eq. 30 we therefore obtain

$$c_j e^{2\pi im/N} - c_j y + c_j e^{-2\pi im/N} = 0 \tag{A30}$$

$$y = e^{2\pi im/N} + e^{-2\pi im/N} = 2\cos\frac{2m\pi}{N} \tag{A31}$$

The result of Eq. A31 is consistent with that of Eq. 21.

Appendix 2: The derivation of Eq. 18 to give the normalizing constants

The normalizing constant shown in Eq. 18 is derived as follows.

Method 1

$$\left(\sum_{j=1}^{N} \sin^2 j\theta\right)^{-1/2} = \left(\sum_{j=1}^{N} \frac{1-\cos 2j\theta}{2}\right)^{-1/2} = \left(\frac{N}{2} - \frac{1}{2}\sum_{j=1}^{N} \cos 2j\theta\right)^{-1/2} \tag{A32}$$

If we can prove Eq. A33.

$$\sum_{j=1}^{N} \cos 2j\theta = -\cos 0 = -1 \tag{A33}$$

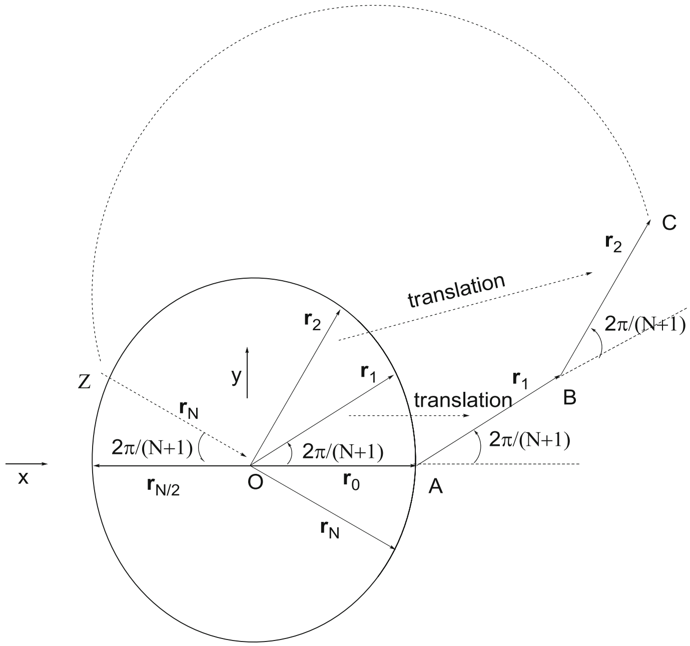


Fig. 6 The N + 1 vectors $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, …, $\mathbf{r}_N$ divide the circle equally and they can form a regular polygon OABC…Z, shown as a dotted line with N + 1 sides. The radius of the circle in the figure is set at unity for simplicity thus $\mathbf{r}_j$ represents a unit vector. Every vector is rotated by an angle of $2\pi/(N+1)$ from the previous vector. The N + 1 vectors rotate through an angle of 2π thus forming the closed N + 1 regular polygon OABC…Z

Then Eq. 18 is obtained as Eq. A34.

$$a_1 = \left(\sum_{j=1}^{N} \sin^2 j\theta \right)^{-1/2} = \left(\frac{N}{2} - \frac{-1}{2} \right)^{-1/2} = \sqrt{\frac{2}{N+1}} \tag{A34}$$

Now we need to prove Eq. A33 and the proof can be based on Fig. 6. As shown in Fig. 6, $\mathbf{r}_0$, $\mathbf{r}_1$,$\mathbf{r}_2$, …, and $\mathbf{r}_N$ form a closed polygon with N + 1 sides so that as a consequence the sum of all the vectors is zero. If the unit vectors are expressed in complex form Eq. A35 is obtained.

$$\sum_{j=0}^{N} \mathbf{r}_j = \sum_{j=0}^{N} \left(\cos \frac{j2\pi}{N+1} + i \sin \frac{j2\pi}{N+1} \right) = \sum_{j=0}^{N} (\cos j\theta + i \sin j\theta) = 0 \tag{A35}$$

Equation A35 signifies that the sum of the real and the imaginary parts should both equal 0. We will ignore the imaginary parts of A35. For the real components, we obtain Eq. A36.

$$\sum_{j=0}^{N} \cos j\theta = \sum_{j=0}^{N} \cos j\frac{2\pi}{N+1} = 1 + \sum_{j=1}^{N} \cos j\frac{2\pi}{N+1} = 1 + \sum_{j=1}^{N} \cos j\theta = 0 \quad \text{(A36)}$$

Equations A36 and A33 are very similar except that the former is in angle units of θ while the latter is in angle units of 2θ. Thus we need to prove Eq. A37 since Eq. A33 can readily be obtained from the real part of Eq. A37.

$$\sum_{j=0}^{N} \mathbf{r}_{2j} = \sum_{j=0}^{N} (\cos 2j\theta + i \sin 2j\theta) = \sum_{j=0}^{N} \left(\cos \frac{2j2\pi}{N+1} + i \sin \frac{2j2\pi}{N+1} \right)$$
$$= 1 + \sum_{j=1}^{N} (\cos 2j\theta + i \sin 2j\theta) = 0 \quad \text{(A37)}$$

We need to prove Eq. A37 for the two possibilities, where N + 1 is odd or even, respectively.

First, when N + 1 is odd: If we pick (N + 1) times every alternate vector from $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, …, $\mathbf{r}_N$ in a circular way in Eq. A37, then Eq. A37 reduces to Eq. A35 since all the N + 1 vectors appear once and only once in the summation of Eq. A37. Taking N + 1 = 5 as an example, there will be 5 vectors, namely $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, $\mathbf{r}_4$ then if we select alternate vectors from the list returning to the start after the final $\mathbf{r}_4$, then on including all vectors once, we obtain Eq. A38.

$$\sum_{i=0}^{4} \mathbf{r}_{2i} = \sum_{j=0}^{4} (\cos 2j\theta + i \sin 2j\theta) = \mathbf{r}_0 + \mathbf{r}_2 + \mathbf{r}_4 + \mathbf{r}_6(= \mathbf{r}_1) + \mathbf{r}_8(= \mathbf{r}_3)$$
$$= \mathbf{r}_0 + \mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \mathbf{r}_4 = \sum_{i=0}^{4} \mathbf{r}_i = 0 \quad \text{(A38)}$$

The real components in Eq. A37 can be simplified as below, thus proving Eq. A33 when N + 1 is odd.

$$\sum_{j=0}^{N} \cos 2j\theta = \cos 0 + \sum_{j=1}^{N} \cos 2j\theta = 1 + \sum_{j=1}^{N} \cos 2j\theta = 0$$

N + 1 is even: If we select N + 1 alternate vectors from $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, …, $\mathbf{r}_N$ in a circular way and sum them, we would sum half of the vectors $\mathbf{r}_x$ (x = even) twice and ignore the rest with x = odd. For example, if there are six vectors in the list $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, $\mathbf{r}_4$, $\mathbf{r}_5$, we have Eq. A39.

$$\sum_{i=0}^{5}\mathbf{r}_{2i} = \sum_{j=0}^{5}(\cos 2j\theta + i\sin 2j\theta) = \mathbf{r}_0 + \mathbf{r}_2 + \mathbf{r}_4 + \mathbf{r}_6(=\mathbf{r}_0) + \mathbf{r}_8(=\mathbf{r}_2) + \mathbf{r}_{10}(=\mathbf{r}_4)$$
$$= 2(\mathbf{r}_0 + \mathbf{r}_2 + \mathbf{r}_4) = \mathbf{r}_0 + \sum_{i=1}^{5}\mathbf{r}_{2i} = 0 \tag{A39}$$

There will be a N/2 regular polygon inside the N + 1 regular polygon if N + 1 is even. Eqs. A35 and A39 are valid irrespective of the value of the length of the vectors when all the vectors are with the same length. So we have proved above that Eq. A37 is valid independent of whether N + 1 is odd or even. By using Eqs. A37, A32, and A33, Eq. A34 which gives the values of the normalizing constants can be easily obtained.

Method 2

The derivation of Eq. A18 for the normalizing constants a_1 is obtained from Eq. A41. Eq. A41 is obtained by using Eq. A40[1]

$$\sum_{j=1}^{N}\frac{2\cos 2j\theta}{2} = \sum_{j=1}^{N}\frac{e^{2i(j\theta)} + e^{-2i(j\theta)}}{2}$$
$$= -\frac{1}{2} + \frac{1}{2}\sum_{j=-N}^{N} e^{2i(j\theta)} = -\frac{1}{2} + \frac{1}{2}\frac{e^{-2i(N\theta)} - e^{i(2N+2)\theta}}{1 - e^{2i\theta}}$$

[1] Eq. A40 can also be derived from the following

$$\sin(2j+1)\theta - \sin(2j-1)\theta = 2\sin\theta\cos 2j\theta$$
$$\sum_{j=-N}^{N} e^{2ij\theta} = 1 + \sum_{j=1}^{N}\left(e^{2ij\theta} + e^{-2ij\theta}\right) = 1 + \sum_{j=1}^{N} 2\cos(2j\theta)$$
$$= 1 + 2\cos(2\theta) + 2\cos(4\theta) + \ldots + 2\cos(2N\theta)$$
$$= 1 + \frac{1}{\sin\theta}\left\{[\sin(3\theta) - \sin\theta] + [\sin(5\theta) - \sin(3\theta)] + \ldots + [\sin((2N+1)\theta) - \sin((2N-1)\theta)]\right\}$$
$$= 1 + \frac{\sin[(2N+1)\theta] - \sin\theta}{\sin\theta} = \frac{\sin[(2N+1)\theta]}{\sin\theta}$$

or more generally

$$\sum_{j=1}^{N}[\cos(2j\theta) + i\sin(2j\theta)] = \sum_{j=1}^{N}\cos(2j\theta) + i\sum_{j=1}^{N}\sin(2j\theta) = \sum_{j=1}^{N} e^{i(2j\theta)} = \frac{e^{i2\theta}(1 - e^{i2N\theta})}{1 - e^{i2\theta}}$$
$$= \frac{e^{i\theta}e^{iN\theta}(e^{-iN\theta} - e^{iN\theta})}{e^{-i\theta} - e^{i\theta}} = \left\{\cos[(N+1)\theta] + i\sin(N+1)\theta]\right\}\frac{-2i\sin(N\theta)}{-2i\sin\theta}$$
$$= \frac{\cos[(N+1)\theta]\sin(N\theta)}{\sin\theta} + i\frac{\sin[(N+1)\theta]\sin N\theta}{\sin\theta}$$

The real part of the above equation leads to Eq. A40.

$$
\begin{aligned}
&= -\frac{1}{2} + \frac{1}{2}\frac{e^{-i(2N+1)\theta} - e^{i(2N+1)\theta}}{e^{-i\theta} - e^{i\theta}} = \frac{1}{2}\frac{\sin(2N+1)\theta - \sin\theta}{\sin\theta} \\
&= \frac{1}{2}\frac{2\cos(N+1)\theta\sin N\theta}{\sin\theta}
\end{aligned}
\tag{A40}
$$

From Eq. A40, Eq. A41 is obtained.

$$
\begin{aligned}
\left(\sum_{j=1}^{N}\sin^2 j\theta\right)^{-1/2} &= \left(\sum_{j=1}^{N}\frac{1-\cos 2j\theta}{2}\right)^{-1/2} = \left(\frac{N}{2} - \frac{1}{2}\sum_{j=1}^{N}\cos 2j\theta\right)^{-1/2} \\
&= \left(\frac{N}{2} - \frac{\cos(N+1)\frac{m\pi}{N+1}\sin N\frac{m\pi}{N+1}}{2\sin\frac{m\pi}{N+1}}\right)^{-1/2} \\
&= \left(\frac{N}{2} - \cos m\pi\frac{\sin\frac{Nm\pi}{N+1}}{2\sin\frac{m\pi}{N+1}}\right)^{-1/2} \\
&= \left(\frac{N}{2} + (-1)^{m+1}\frac{\sin(m\pi - \frac{m\pi}{N+1})}{2\sin\frac{m\pi}{N+1}}\right)^{-1/2} \\
&= \left(\frac{N}{2} + (-1)^{m+1}\frac{(-1)^{m+1}}{2}\right)^{-1/2} = \left(\frac{2}{N+1}\right)^{1/2}
\end{aligned}
\tag{A41}
$$

Appendix 3: Applications

Application 1: Benzene

The strategy used in Sect. 4 for straight chain polyenes when N is even, can be used here for benzene. Note that there are N atoms in a conjugated system though the calculation of the normalizing constants in the straight chain polyene in method 1 of "Appendix 2" involves N+1 since $\mathbf{r}_0$ is included. The relevant coefficients are shown in Fig. 7a. The boundary conditions are created by joining the two end atoms together [indicated by a dotted line in Fig. 7a]. Using Eq. 30 and taking one of the terminal atoms as the central atom we obtain Eq. A42 as the boundary conditions for the symmetric wave function.

$$
\begin{aligned}
&\mathrm{c}_{-5/2} + \mathrm{c}_{3/2} = 2\cos\theta\cdot\mathrm{c}_{5/2} \\
&\cos\frac{5}{2}\theta + \cos\frac{3}{2}\theta = 2\cos\theta\cdot\cos\frac{5}{2}\theta = \cos\left(\frac{5}{2}\theta + \theta\right) + \cos\left(\frac{5}{2}\theta - \theta\right)
\end{aligned}
\tag{A42}
$$

Solving Eq. A42, we have

$$
\cos\frac{7}{2}\theta - \cos\frac{5}{2}\theta = 0; \quad -2\sin 3\theta\sin\frac{1}{2}\theta = 0; \theta = \frac{m\pi}{3}; \quad m = 0, 1, 2 \tag{A43}
$$

For the anti-symmetric function, Eq. A44 is given from the boundary condition from one of the two terminal atoms in Fig. 7a. In Eq. A45, θ cannot be zero, or an empty wave function results.

$$\begin{gathered} c_{3/2} + c_{-5/2} = 2\cos\theta \cdot c_{5/2} \\ \sin\frac{3}{2}\theta - \sin\frac{5}{2}\theta = 2\cos\theta \cdot \sin\frac{5}{2}\theta = \sin\left(\frac{5}{2}\theta + \theta\right) + \sin\left(\frac{5}{2}\theta - \theta\right) \end{gathered} \tag{A44}$$

Solving Eq. A44, we have

$$\begin{aligned} &\sin\frac{7}{2}\theta + \sin\frac{5}{2}\theta = 0; \qquad 2\sin 3\theta\cos\frac{1}{2}\theta = 0 \\ &\theta = \frac{m\pi}{3}; \qquad m = 1, 2, 3 \end{aligned} \tag{A45}$$

The strategy used in Sect. 5 for a straight chain polyene when N is odd can alternatively be used here for benzene. Benzene can be obtained by superimposing the first and last atoms in Fig. 7b. The relevant coefficients are also shown there. The boundary conditions are derived by taking the superimposed atoms as the central atom. The results are shown from Eqs. A46–A50. In Eq. A50, θ cannot be 0, or a empty wave function results. For symmetric orbitals, we have

$$\begin{gathered} C_2 + C_{-2} = 2\cos\theta C_3 \\ \cos 2\theta + \cos 2\theta = 2\cos\theta \cdot \cos 3\theta \end{gathered} \tag{A46}$$

since

$$2\cos\theta \cdot \cos 3\theta = \cos 4\theta + \cos 2\theta \tag{A47}$$

By combining Eqs. A46 and A47, we obtain

$$\begin{aligned} &\cos 4\theta - \cos 2\theta = 0; \quad -2\sin 3\theta\sin\theta = 0; \\ &\theta = \frac{m\pi}{3}; \quad m = 0, 1, 2, 3 \end{aligned} \tag{A48}$$

For anti-symmetric orbitals, we obtain

$$\begin{aligned} &\sin 2\theta - \sin 2\theta = 2\cos\theta \cdot \sin 3\theta; \\ &\sin 3\theta = -\sin 3\theta; \text{ or } c_3 = -c_{-3}; \end{aligned} \tag{A49}$$

Both equations shown in Eq. A49 lead to Eq. A50.

$$2\sin 3\theta = 0; \quad \theta = \frac{m\pi}{3}; \quad m = 1, 2, 3 \tag{A50}$$

The fact that the trigonometric treatment can be applicable in such a general way indicates that the Hückel theory for conjugated π orbital systems is really rooted in the more general theory of Fourier series expansion.

Application 2: Benzyl radical

For the symmetric wave function, the coefficient c_x (Fig. 8) on the terminal carbon, x, can be calculated from Eq. 33 as shown in Eq. A51

$$\begin{aligned} c_2 + c_{-2} + c_x &= 2\cos\theta \cdot c_3 \\ \cos 2\theta + \cos 2\theta + c_x &= 2\cos\theta\cos 3\theta \\ 2\cos\theta\cos 3\theta &= \cos 4\theta + \cos 2\theta \end{aligned} \tag{A51}$$

Therefore

$$c_x = \cos 4\theta - \cos 2\theta \tag{A52}$$

And θ for the symmetric orbitals can be obtained from the boundary condition that $c_{x+1} = 0$ and the derivation is given in Eqs. A53–A54 (Fig. 8).

$$2c_x\cos\theta = \cos 3\theta + c_{x+1} \tag{A53}$$

$$\begin{aligned} &2\cos\theta\,(\cos 4\theta - \cos 2\theta) = \cos 3\theta + 0 = \cos(\theta + 2\theta) \\ &2\cos\theta\left\{2[(2\cos^2\theta - 1)^2 - 1] - (2\cos^2\theta - 1)\right\} \\ &= \cos\theta(2\cos^2\theta - 1) - 2(1 - \cos^2\theta)\cos\theta \\ &\cos\theta(16\cos^4\theta - 24\cos^2\theta + 7) = 0 \\ &2\cos\theta = 0, \pm\sqrt{(3 \pm \sqrt{2})} \end{aligned} \tag{A54}$$

The other two anti-symmetric orbitals can be obtained easily using the boundary condition $\sin 3\theta = 0$ or $2\cos\theta \cdot \sin 2\theta = \sin\theta + 0$. This results in a total of seven orbitals for symmetric and antisymmetric orbitals.

Application 3: Naphthalene

The orbitals of naphthalene can be sorted into four groups as (S_x, S_y), (A_x, A_y), (S_x, A_y), and (A_x, S_y), which represent symmetric (S) or anti-symmetric (A) orbitals about x and y axes as shown in Fig. 9. There are 10 orbitals in total. The boundary conditions originate from either of the central atoms at position 9 or 10.

A guideline is provided as follows

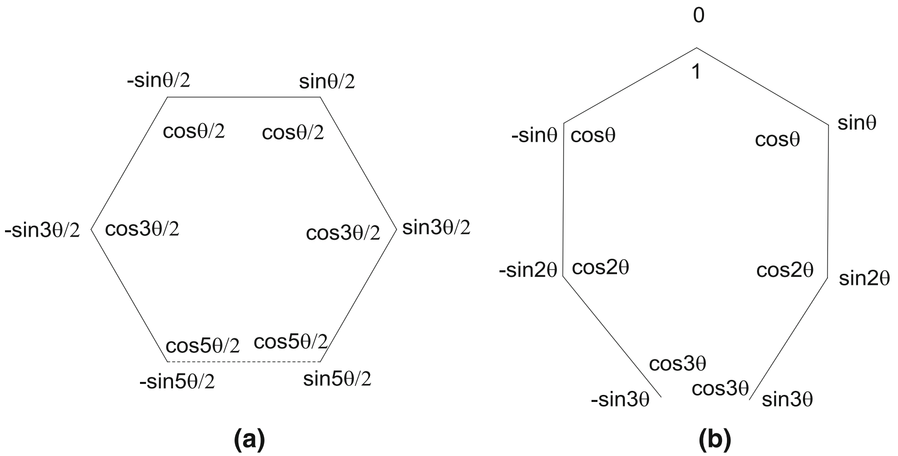


Fig. 7 Coefficients for benzene from two different models of chain polyenes. As an acyclic system N = 6 (**a**) and as an acyclic system N = 7 (**b**), respectively. Every atom provides an atomic orbital and an electron

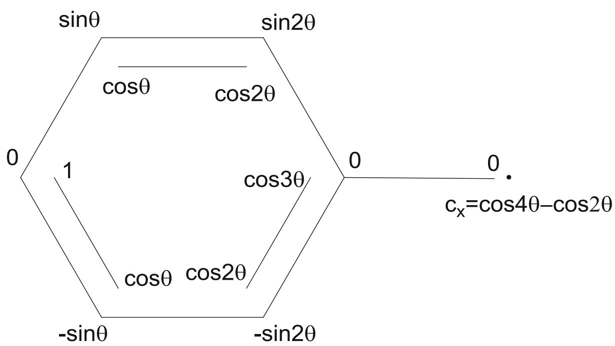


Fig. 8 Coefficients for benzyl radical. Every atom provides an atomic orbital and an electron

Derivation of (S_x, S_y)

For (S_x, S_y), the $2\cos\theta$ values are obtained from the boundary conditions where atom 9 or 10 is taken as the middle atom. Using Eq. 33 with $c_{5/2} + c_{3/2} + c_{3/2} = 2\cos\theta c_{5/2}$

$$\begin{aligned}
&2\cos\frac{3}{2}\theta + \cos\frac{5}{2}\theta = 2\cos\theta\cos\frac{5}{2}\theta = \cos\frac{7}{2}\theta + \cos\frac{3}{2}\theta \\
&\cos\frac{7}{2}\theta - \cos\frac{5}{2}\theta = \cos\frac{3}{2}\theta \\
&\cos\frac{3}{2}\theta = -2\sin 3\theta\sin\frac{1}{2}\theta = -4\sin\frac{3}{2}\theta\cos\frac{3}{2}\theta\sin\frac{1}{2}\theta \\
&\cos\frac{3}{2}\theta\left(1 + 4\sin\frac{3}{2}\theta\sin\frac{1}{2}\theta\right) = 0
\end{aligned} \tag{A55}$$

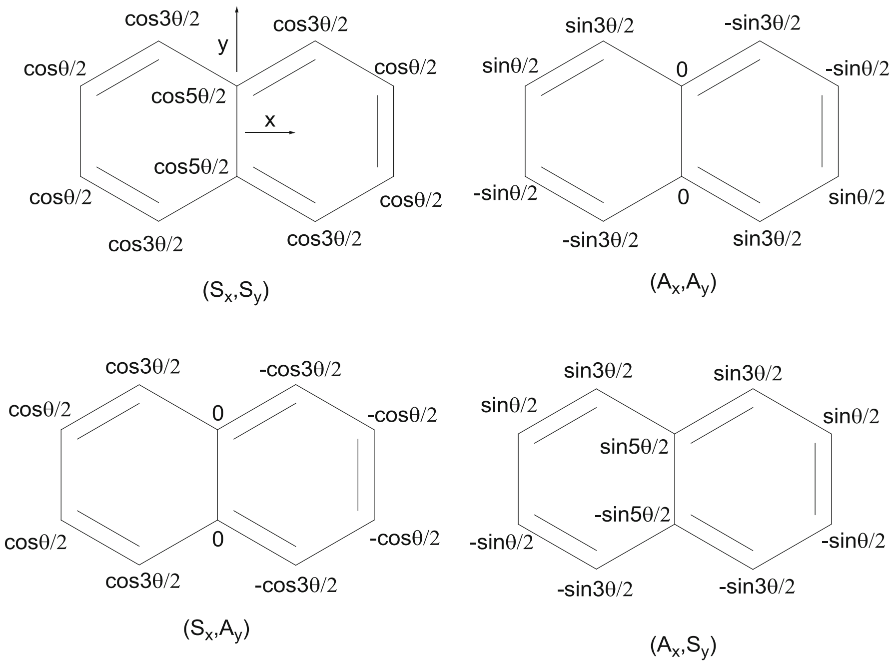


Fig. 9 Coefficients for naphthalene

$$\cos\frac{3}{2}\theta[1+2(\cos\theta-\cos 2\theta)]=0 \tag{A56}$$

Equation A56 requires the two factors to be zero. First

$$\begin{aligned}1+2(\cos\theta-\cos 2\theta)&=0\\ \cos\theta-2\cos^2\theta+1&=-\frac{1}{2}\\ \left(\sqrt{2}\cos\theta-\frac{1}{2\sqrt{2}}\right)^2&=\frac{13}{8}\\ 2\cos\theta&=\frac{1}{2}(1\pm\sqrt{13})\end{aligned} \tag{A57}$$

second, Eq. A56 requires Eq. A58 to be met.

$$\cos\frac{3}{2}\theta=\cos\left(\theta+\frac{1}{2}\theta\right)=0 \tag{A58}$$

$$\begin{aligned}&\cos\frac{1}{2}\theta\cos\theta-\sin\frac{1}{2}\theta\sin\theta=0\\ &\cos\frac{1}{2}\theta\left(2\cos^2\frac{1}{2}\theta-1\right)-2\sin^2\frac{1}{2}\theta\cos\frac{1}{2}\theta=0\\ &4\cos^3\frac{1}{2}\theta-3\cos\frac{1}{2}\theta=\cos\frac{1}{2}\theta\left(4\cos^2\frac{1}{2}\theta-3\right)=0;\quad \cos^2\frac{1}{2}\theta=\frac{3}{4}\end{aligned}$$

$$\cos\theta = 2\cos^2\frac{1}{2}\theta - 1 = 2\times\frac{3}{4} - 1 = \frac{1}{2};\quad 2\cos\theta = 1 \tag{A59}$$

An alternative derivation of (S_x, S_y)

From Eq. A55

$$\begin{aligned}
&\cos\left(\frac{5}{2}\theta+\theta\right) = \cos\left(\frac{1}{2}\theta+\theta\right) + \cos\left(\frac{3}{2}\theta+\theta\right)\\
&\cos\frac{5}{2}\theta\cos\theta - \sin\frac{5}{2}\theta\sin\theta = \left(\cos\frac{1}{2}\theta\cos\theta - \sin\frac{1}{2}\theta\sin\theta\right)\\
&+\left(\cos\frac{3}{2}\theta\cos\theta - \sin\frac{3}{2}\theta\sin\theta\right)\\
&\cos\theta\left(\cos\frac{5}{2}\theta - \cos\frac{3}{2}\theta - \cos\frac{1}{2}\theta\right) = \sin\theta\left(\sin\frac{5}{2}\theta - \sin\frac{3}{2}\theta - \sin\frac{1}{2}\theta\right)\\
&\cos\theta\left(-2\sin2\theta\sin\frac{1}{2}\theta - \cos\frac{1}{2}\theta\right) = \sin\theta\left(2\cos2\theta\sin\frac{1}{2}\theta - \sin\frac{1}{2}\theta\right)
\end{aligned}\tag{A60}$$

Taking the left hand side of Eq. A60, we obtain

$$\begin{aligned}
&\left(2\cos^2\frac{1}{2}\theta - 1\right)\left(-8\sin^2\frac{1}{2}\theta\cos\frac{1}{2}\theta\left(2\cos^2\frac{1}{2}\theta-1\right) - \cos\frac{1}{2}\theta\right)\\
&= \left(2\cos^2\frac{1}{2}\theta - 1\right)\left(-16\sin^2\frac{1}{2}\theta\cos^3\frac{1}{2}\theta + 8\sin^2\frac{1}{2}\theta\cos\frac{1}{2}\theta - \cos\frac{1}{2}\theta\right)\\
&= -32\sin^2\frac{1}{2}\theta\cos^5\frac{1}{2}\theta + 32\sin^2\frac{1}{2}\theta\cos^3\frac{1}{2}\theta - 2\cos^3\frac{1}{2}\theta\\
&\quad -8\sin^2\frac{1}{2}\theta\cos\frac{1}{2}\theta - \cos\frac{1}{2}\theta
\end{aligned}$$

Taking the right hand side of Eq. A60, we obtain

$$\begin{aligned}
&2\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta\left\{2\left[2\left(2\cos^2\frac{1}{2}\theta-1\right)^2-1\right]\sin\frac{1}{2}\theta - \sin\frac{1}{2}\theta\right\}\\
&= 2\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta\left(16\cos^4\frac{1}{2}\theta\sin\frac{1}{2}\theta - 16\cos^2\frac{1}{2}\theta\sin\frac{1}{2}\theta + \sin\frac{1}{2}\theta\right)\\
&= 32\cos^5\frac{1}{2}\theta\sin^2\frac{1}{2}\theta - 16\cos^3\frac{1}{2}\theta\sin^2\frac{1}{2}\theta + 2\cos\frac{1}{2}\theta\sin^2\frac{1}{2}\theta
\end{aligned}$$

Equating the two sides of Eq. A60, we obtain

$$\begin{aligned}
&64\cos^6\frac{1}{2}\theta - 128\cos^4\frac{1}{2}\theta + 72\cos^3\frac{1}{2}\theta - 9 = 0\\
&\cos\frac{\theta}{2} = \sqrt{\frac{1+\cos\theta}{2}}
\end{aligned}$$

$$\begin{aligned}
&8(1+\cos\theta)^3 - 32(1+\cos\theta)^2 + 36(1+\cos\theta) - 9 = 0\\
&8\cos^3\theta - 8\cos^2\theta - 4\cos^2\theta + 3 = 0\\
&(2\cos\theta - 1)\left(4\cos^2\theta - 2\cos\theta - 3\right) = 0\\
&4\cos^2\theta - 2\cos\theta - 3 = 0
\end{aligned} \tag{A61}$$

These give the same results for θ as given in Eqs. A57 and A59.

Derivation of (A_x, S_y)

$$\begin{aligned}
&2\sin\frac{3}{2}\theta - \sin\frac{5}{2}\theta = 2\cos\theta\sin\frac{5}{2}\theta = \sin\frac{7}{2}\theta + \sin\frac{3}{2}\theta\\
&\sin\frac{3}{2}\theta = \sin\frac{7}{2}\theta + \sin\frac{5}{2}\theta = 2\sin 3\theta\cos\frac{1}{2}\theta = 4\sin\frac{3}{2}\theta\cos\frac{3}{2}\theta\cos\frac{1}{2}\theta\\
&\sin\frac{3}{2}\theta\left(1 - 4\cos\frac{3}{2}\theta\cos\frac{1}{2}\theta\right) = 0\\
&2(\cos 2\theta + \cos\theta) - 1 = 0\\
&2(2\cos^2\theta - 1) + 2\cos\theta - 1 = 0\\
&2\cos\theta = \frac{-1 \pm \sqrt{13}}{2}
\end{aligned} \tag{A62}$$

$$\begin{aligned}
&\sin\frac{3}{2}\theta = \sin\left(\frac{1}{2}\theta + \theta\right) = 0\\
&\sin\theta\cos\frac{1}{2}\theta + \cos\theta\sin\frac{1}{2}\theta = 2\sin\frac{1}{2}\theta\cos^2\frac{1}{2}\theta + \left(2\cos^2\frac{1}{2}\theta - 1\right)\sin\frac{1}{2}\theta\\
&= \sin\frac{1}{2}\theta\left(2\cos^2\frac{1}{2}\theta + 2\cos^2\frac{1}{2}\theta - 1\right) = 0\\
&2(2\cos^2\frac{1}{2}\theta - 1) + 1 = 0; \quad 2\cos\theta = -1
\end{aligned} \tag{A63}$$

Derivation of (A_x, A_y)

For (A_x, A_y), the $2\cos\theta$ values are obtained from the boundary conditions with Eq. A64.

$$\begin{aligned}
&\sin\frac{1}{2}\theta + 0 = 2\cos\theta\sin\frac{3}{2}\theta = \sin\frac{5}{2}\theta + \sin\frac{1}{2}\theta\\
&\sin\frac{5}{2}\theta = 0; \quad \theta = \frac{2m\pi}{5}; \quad m = 1, 2
\end{aligned} \tag{A64}$$

Derivation of (S_x, A_y)

$$\cos\frac{1}{2}\theta + 0 = 2\cos\theta\cos\frac{3}{2}\theta = \cos\frac{5}{2}\theta + \cos\frac{1}{2}\theta$$
$$\cos\frac{5}{2}\theta = 0; \quad \theta = \frac{(2m+1)\pi}{5}; \quad m = 0, 1 \tag{A65}$$

To calculate the energy of the orbitals, the value of $2\cos\theta$ is required. The analytical form of the relevant $2\cos\theta$ where $\theta = \pi/5$ is obtained in 'Appendix 4".

Appendix 4: Calculation of $\cos\frac{\pi}{5}$

Method 1

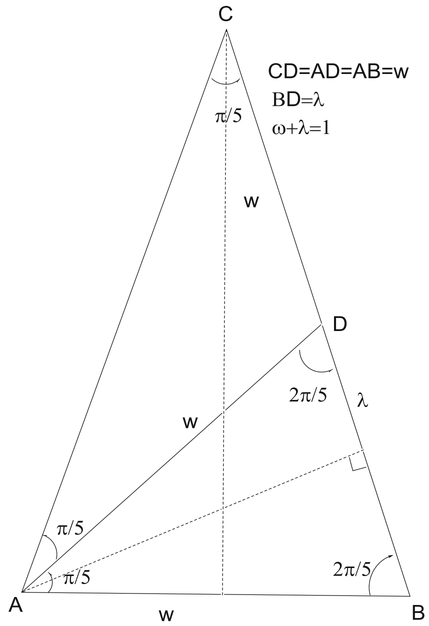
$$\cos\frac{3\pi}{5} = -\cos\left(\pi - \frac{3\pi}{5}\right) = -\cos\frac{2\pi}{5} = -\left(2\cos^2\frac{\pi}{5} - 1\right)$$
$$\cos\frac{3\pi}{5} = \cos\left(\frac{2\pi}{5} + \frac{\pi}{5}\right) = \cos\frac{2\pi}{5}\cos\frac{\pi}{5} - \sin\frac{2\pi}{5}\sin\frac{\pi}{5} = -\left(2\cos^2\frac{\pi}{5} - 1\right)$$
$$\left(2\cos^2\frac{\pi}{5} - 1\right)\cos\frac{\pi}{5} - 2\left(1 - \cos^2\frac{\pi}{5}\right)\cos\frac{\pi}{5} = -2\cos^2\frac{\pi}{5} + 1$$
$$4\cos^3\frac{\pi}{5} + 2\cos^2\frac{\pi}{5} - 3\cos\frac{\pi}{5} - 1 = 0$$
$$\left(\cos\frac{\pi}{5} + 1\right)\left(4\cos^2\frac{\pi}{5} - 2\cos\frac{\pi}{5} - 1\right) = 0$$
$$4\cos^2\frac{\pi}{5} - 2\cos\frac{\pi}{5} - 1 = 0$$
$$2\cos\frac{\pi}{5} = \frac{1+\sqrt{5}}{2}$$

Method 2

$$\cos\frac{4\pi}{5} = -\cos\frac{\pi}{5}$$
$$\left[2\left(2\cos^2\frac{\pi}{5} - 1\right)^2 - 1\right] + \cos\frac{\pi}{5} = 0$$
$$8\cos^4\frac{\pi}{5} - 8\cos^2\frac{\pi}{5} + \cos\frac{\pi}{5} + 1 = 0$$
$$\left(2\cos^2\frac{\pi}{5} + \cos\frac{\pi}{5} - 1\right)\left(4\cos^2\frac{\pi}{5} - 2\cos\frac{\pi}{5} - 1\right) = 0$$
$$4\cos^2\frac{\pi}{5} - 2\cos\frac{\pi}{5} - 1 = 0$$

The result is the same as that obtained in method 1.

Fig. 10 Calculation of $\cos \pi/5$ by geometric methods



Method 3

In Fig. 10, △ABC ∼ △ABD

$$\frac{BC}{AB} = \frac{AB}{BD}; \frac{1}{w} = \frac{w}{1-w}$$

$$w^2 + w - 1 = 0; \quad w = \frac{\sqrt{5}-1}{2}$$

$$\lambda = DB = 1 - w = \frac{3-\sqrt{5}}{2}$$

$$\cos\frac{2\pi}{5} = \frac{\frac{1}{2}AB}{BC} = \frac{\frac{1}{2}BD}{AB} = \frac{\sqrt{5}-1}{4}$$

$$-\cos\frac{\pi}{5} = \cos\frac{4\pi}{5} = 2\cos^2\frac{2\pi}{5} - 1 = -\frac{\sqrt{5}+1}{2}$$

Appendix 5: Derivation of Eq. 26

For a cyclic conjugated polyene, the boundary (or periodic) condition is

$$\mathrm{c_j} = \mathrm{c_{N+j}}$$
$$(c_{N+j})/c = \sin[(N+j)\theta + \omega] = \sin[(N\theta + \omega) + j\theta]$$

$$= \sin(N\theta + \omega)\cos j\theta + \sin j\theta \cos(N\theta + \omega) \tag{A66}$$

since cos(N$\theta + \omega$) can be either positive or negative within the interval 0 to π, we obtain

$$\begin{aligned} \cos(N\theta + \omega) &= \pm[1 - \sin^2(N\theta + \omega)]^{1/2} \\ &= \pm\left[1 - \sin^2\left(N\frac{2m\pi}{N} + \omega\right)\right]^{1/2} = \pm(1 - \sin^2\omega)^{1/2} \\ &= \pm\cos\omega \end{aligned} \tag{A67}$$

By inserting Eq. A67 into Eq. A66, we obtain

$$(c_{N+j})/c = \sin\omega\cos j\theta \pm \sin j\theta\cos\omega \tag{A68}$$

for the plus sign in Eq. A68, we obtain

$$\begin{aligned} (c_{N+j})/c &= \sin[(N + j)\theta + \omega] = \sin\omega\cos j\theta + \sin j\theta\cos\omega \\ &= \sin(j\theta + \omega) = \sin(j\theta + \omega) = c_j \end{aligned} \tag{A69}$$

for the minus sign in Eq. A68, we obtain the identity transformation

$$\begin{aligned} (c_{N+j})/c &= \sin[(N + j)\theta + \omega] = \sin\omega\cos j\theta - \sin j\theta\cos\omega \\ &= \sin(\pi - \omega)\cos j\theta + \sin j\theta\cos(\pi - \omega) \\ &= \sin(\pi - \omega + j\theta) = \sin(j\theta + \omega) = c_j \end{aligned} \tag{A70}$$

Thus Eq. 26 is proven and Eq. A70 requires Eq. 27 to be satisfied.

References

1. J.M. LoBue, J. Chem. Educ. **79**(11), 1378 (2002)
2. R.M. Hanson, J. Chem. Educ. **79**(11), 1379 (2002)
3. M.A. Fox, F.A. Matsen, J. Chem. Educ. **62**(6), 477 (1985)
4. S. Humbel, J. Chem. Educ. **84**(6), 1056 (2007)
5. Y. Liu, B. Liu, Y. Liu, M.G.B. Drew, Chem. Educator **16**, 202–205 (2011)
6. M.R. Hoffmann, J. Phys. Chem. **100**(15), 6125–6130 (1996)
7. G. Bor, S.F.A. Kettle, J. Chem. Educ. **76**(12), 1723–1726 (1999)
8. E. Kumpinsky, Ind. Eng. Chem. Res. **31**(1), 440–445 (1992)
9. F.A. Cotton, *Chemical Applications of Group Theory*, 3rd edn. (Wiley, London, 1990), pp. 152–157
10. L. Salem, *The Molecular Orbital Theory of Conjugated System* (W.A. Benjamin, New York, 1966)
11. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961)
12. C. Kittel, *Introduction to Solid State Physics*, 8th edn. (Wiley, New York, 2005), pp. 39–42
13. G. Grosso, G.P. Parravicini, *Solid State Physics* (Academic Press, Elsevier Science, Amsterdam, 1999), pp. 1–3
14. G. Grosso, G.P. Parravicini, *Solid State Physics* (Academic Press, Elsevier Science, Amsterdam, 1999), pp. 16–18
15. Y. Öhrn, *Elements of Molecular Symmetry* (Wiley, London, 2000), pp. 189–190
16. D.M. Bishop, *Group Theory and Chemistry* (Dover Publications, New York, 1973), pp. 212–214

17. J.D. Patterson, B.C. Bailey, *Solid-state Physics, Introduction to the Theory* (Springer, Berlin, 2007), pp. 178–181
18. J.B. Dence, *Mathematical Techniques in Chemistry* (Wiley, New York, 1975), pp. 239–242
19. K.F. Riley, M.P. Hobson, S.J. Bence, *Mathematical Methods for Physics and Engineering*, 3rd edn. (Cambridge University Press, Cambridge, 2006), pp. 11–15
20. Y. Liu, B. Liu, Y. Liu, M.G.B. Drew, J. Chem. Educ. **89**(3), 355–359 (2012)
21. Y. Liu, B. Liu, Y. Liu, M.G.B Drew, J. Math Chem. **49**(9), 2089–2108 (2011)
22. Y. Liu, Y. Liu, M.G.B. Drew, Chem. Educator **17**, 118–124 (2012)
23. Y. Liu, M.G.B. Drew, Y. Liu, Mater. Chem. Phys. **134**, 266–272 (2012)