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ORIGINAL PAPER

Phased cycles

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Abstract We define a *phased* graph G to yield an adjacency matrix $A(G)$ having general magnitude-1 values in the same locations as the usual unphased case, but subject to the restriction that A be Hermitian. Some characteristics of phased cycles, their eigenspectra, their symmetry, and their net energy are contemplated and described.

Keywords Phases · Phased graph · Phased cycle · Eigensolution · Symmetry

1 Introduction

A *phased* graph G is one with a phased adjacency matrix $A = [a_{uv}]_{u,v=1}^{n}$ having weights $a_{uv} = e^{i\theta_{uv}}$, where $\theta_{vu} = -\theta_{uv} \in \mathbb{R}$. Thence, A is Hermitian, and so is diagonalizable with real eigenvalues. Such matrices are realized in a few different physico-chemical contexts, as indicated in [1].

Here, we treat in some detail the case that G is an n-cycle. The eigenvalues (and eigenvectors) are neatly determined, what symmetries of the unphased case might be preserved are identified, and the total energies for the system are developed. This work constitutes a generalization of the simple (unphased) cycle in a way that is somewhat different than the very extensively studied idea of "circulant" matrices [2], where cyclic symmetry is manifestly preserved while allowing interconnections of general (cyclically symmetric) weights.

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We follow common notation and ideas. In particular, the *chemical* energy $\varepsilon_0(G)$ represents the Hückel-type ground-state energy, for a number of electrons matching the number n of sites. That is $\varepsilon_0(G)$ is the sum over $n_j\lambda_j$ where occupation numbers n_j for eigenvalues λ_j are chosen between 0 & 2, so as to maximize $\varepsilon_0(G)$, subject to the constraint that the n_j sum to n. Also, $\varepsilon_{\text{opt}}(G)$ is a maximal positive chemical energy, with no constraint on matching the numbers of sites and electrons, whence the net (molecular) charge q_{opt} may be nonzero, and perhaps depend on the phases. It is understood that for $\varepsilon_{\text{opt}}(G)$ the positive energy orbitals are doubly occupied, and the negative energy orbitals are unoccupied, while 0-energy orbitals are singly occupied. In addition to the values of these different total energies, a natural question concerns when $q_{\text{opt}} = 0$.

2 Eigensolution

For the phased n-cycle C_n, with edge set $E(C_n) = \{\{j, j+1\} \mid j \in [1, n]\}$ where $[1, n] := \{1, 2, \ldots, n\}$, and addition modulo n of these integers is understood, throughout this paper. A useful invariant turns out to be the *net phase*

$$\theta_0 := \left(\sum_{j+1}^{n} \theta_{j,j+1}\right) \mod 2\pi. \tag{1}$$

Then

Theorem 1 *For a single n-cycle C_n with phased adjacency matrix $A(C_n)$, the eigenvalues are $2\cos\eta_j$ with corresponding (unnormalized) eigenvector having k-th component* $\exp i(k\eta_j - \sum_{l=1}^{k}\theta_{l,l+1})$, *where $\eta_j = (\theta_0 + 2\pi j)/n$ for the j-th eigencase, $j \in [0, n-1]$.*

Proof We start considering just the part of $A \equiv A(C_n)$ which connects from vertex j to $(j+1) \mod n$, $j \in [1, n]$. That is, define a matrix $\mathcal{C}$ with (j,k)-th entry $= 0$ except when $k = j+1$, whence the value is $e^{i\theta_{j,j+1}}$. Further, consider the possibility that the eigenproblem for $\mathcal{C}$ with the eigenvector $\vec{c}$ has the j-th component $e^{i\varphi_j}$, and eigenvalue $e^{i\eta}$. Then,

$$e^{i(\theta_{j,j+1}+\varphi_{j+1})} = e^{i(\eta+\varphi_j)}, \quad j \in [1, n]$$

so that given the $\theta_{j,j+1}(j \in [1, n])$, and φ_1, we recursively determine $\varphi_2, \varphi_3, \ldots, \varphi_n$ & η to satisfy these equations. Thence (say, with $\varphi_1 = 0$),

$$\theta_{j,j+1} + \varphi_{j+1} \doteqdot \eta + \varphi_j, \quad j \in [1, n-1],$$

where $\doteqdot$ is understood to mean an equality which could be modified by adding an integer multiple of 2π. Use of this relation as a recursion for φ_{j+1} in terms of φ_j gives

$$\varphi_{j+1} \doteqdot j\eta - \sum_{l=1}^{j} \theta_{l,l+1} + j\varphi_1.$$

For the case $j = n$, one has

$$e^{i(\theta_{n,1}+\varphi_1)} = e^{i(\eta+\varphi_n)} = e^{i(n\eta+(n-1)\varphi_1-\sum_{l=1}^{n-1}\theta_{l,l+1})},$$

giving $e^{in\eta} = e^{i(\theta_0-(n-2)\varphi_1)}$. Choosing $\varphi_1 = 0$, we may take

$$\eta = \frac{\theta_0}{n} + 2\pi\frac{l}{n}, \quad l \in [1, n],$$

whence we have achieved $\mathcal{C}\vec{c} = e^{i\eta}\vec{c}$, where $c_j = e^{i\varphi_j}$ and $c_{jk} = e^{i\theta_{j,j+1}}\delta_{k,j+1}$. Now, also

$$e^{i\theta_{j,j-1}}c_{j-1} = e^{i(-\theta_{j-1,j}+\varphi_{j-1})} = e^{i(\varphi_j-\eta)} = e^{-i\eta}c_j,$$

whence $\mathcal{C}^\dagger\vec{c} = e^{-i\eta}\vec{c}$, $A = \mathcal{C}^\dagger + \mathcal{C}$, and $A\vec{c} = 2\cos\eta\cdot\vec{c}$. □

This extends the standard result for the unphased cycle (given by Hückel [3]) and the $\theta_0 = \pi$ phased cycle (by Heilbronner [4]). Moreover, as a direct consequence of this, an extension of the "pictorial" result of Frost and Musulin [5] for the unphased case as well as the $\theta_0 = \pi$ phased case (by Zimmermann [6]) follows:

Corollary 1.1 *The eigenvalues of A for the phased n-cycle are the real parts of n points equiangularly distributed around the $|z| = 2$ circle in the complex plane. At $\theta_0 = 0$, the maximum eigenvalue sits at the intersection of this $|z| = 2$ circle with the positive real axis. The eigenvalues vary continuously with θ_0 such that the n points on the $|z| = 2$ circle are rotated through an angle θ/n from the unphased ($\theta_0 = 0$) position.*

This diagrammatic construction orients the positive real axis downwards (thereby correlating with common orbital energy-level diagrams – where the + direction is upward but with eigenvalues multiplied by a negative parameter).

3 Symmetry

Without phasing, the problem is often elegantly solved through reference to (cyclic or dihedral) symmetry, as eg. in [2]. Thence, one might wonder whether such symmetry ideas apply in the case with a general distribution of phases.

Theorem 2 *Let C_n be an n-cycle with phased adjacency matrix $A \equiv A(C_n)$. Then, the $n \times n$ matrix C with all entries 0 except $c_{j,j+1} \equiv e^{i(\theta_{j,j+1}-\theta_0)/n}$ generates a cyclic group $\mathcal{G} = \{\mathsf{C}^j \mid j \in [1, n]\}$ commuting with A. Also, $A = e^{i\theta_0/n}\mathsf{C}+e^{-i\theta_0/n}\mathsf{C}^\dagger$, which can be expressed in terms of the irreducible idempotents $\mathcal{O}_k$ (corresponding to irreducible characters $\chi_k(\mathsf{C}^{-j}) = e^{i\pi jk/n}$) of the group algebra of $\mathcal{G}$ as $A = \sum_j \lambda_j\mathcal{O}_j$ with the $\lambda_j = 2\cos[(\theta_0 + 2\pi j)/n]$ being eigenvalues of A.*

Proof If we let $\mathcal{C}$ be as in the proof of Theorem 1, then $\mathsf{C} = e^{-i\theta_0/n}\mathcal{C}$ and $\mathsf{C}^n = e^{-i\theta_0}\mathcal{C}^n = I$. But it is readily seen that $\mathcal{C}^n$ is diagonal, with a common value $= \exp(i\sum_{j=1}^{n}\theta_{j,j+1})$, which is just $e^{i\theta_0}$. Thus, $\mathsf{C}^n = I$, and $\{\mathsf{C}^j \mid j \in [1,n]\} \equiv \mathcal{G}$ forms a group, evidently with

$$A = e^{i\theta_0/n}\mathsf{C} + e^{-i\theta_0/n}\mathsf{C}^{-1}.$$

Now, the group elements may be expressed in terms of the primitive (irreducible) idempotents of the group algebra of $\mathcal{G}$—these idempotents being well-known to be given as

$$\mathcal{O}_l = \frac{1}{n}\sum_{j=1}^{n} e^{-2\pi ilj/n}\mathsf{C}^j.$$

See, e.g., [7] with $e^{i2\pi jl/n} = \chi_l(\mathsf{C}^{-j})$ being the (also well-known) l-th irreducible character for C^{-j}. The desired (also well-known) "converse" relation is

$$\mathsf{C}^j = \sum_{l=1}^{n} e^{2\pi ilj/n}\mathcal{O}_l,$$

whence

$$A = \sum_{l=1}^{n}(e^{i(\theta_0+2\pi lj)/n} + e^{-i(\theta_0+2\pi lj)/n})\cdot\mathcal{O}_l = \sum_{l=1}^{n} 2\cos\eta_l\cdot\mathcal{O}_l.$$

□

Thence, at least part of the automorphism group of the unphased n-cycle is retained as a "phased" cyclic group $\mathcal{G}$. But the unphased graph manifests additional involutory elements (viewable as corresponding to reflections normal to the "molecular plane" of a standard planar embedding of the graph). Wherefrom, a question arises as to what happens in the phased case with the additional involutory elements of the phased automorphism group.

Proposition 3 *Let C_n be a phased single cycle with a net phase θ_0 and C as in Proposition 2. Then, a further nonzero $n\times n$ involutory matrix σ satisfying $\sigma\mathsf{C} = \mathsf{C}^{-1}\sigma$ & $\sigma A(C_n) = A(C_n)\sigma$ is excluded except at $\theta_0 = 0$ or π, where the $n\times n$ matrix σ is $= 0$ except the elements $\sigma_{j,n-j} = e^{i(\theta+s_j-s_k)}$, where $s_j := \sum_{l=1}^{j}\theta_{l,l+1}$.*

Proof Any such σ augmenting $\mathcal{G} = \{\mathsf{C}^n \mid j \in [1,n]\}$ yields $\mathcal{G}\cup\sigma\mathcal{G}$ to be a dihedral group with 2-dimensional irreducible representations induced from the irreducible $\mathcal{O}_l$ with $l \neq 0$, or (when n is even) $n/2$. But associated doubly degenerate eigenvalues to $A(G)$ do not occur so long as $\theta_0 \neq 0, \pi/n$. Thus, such a σ (with a nonzero representation) is precluded except possibly at $\theta_0 = 0$ or π/n (where there are double degeneracies for $n \geq 3$).

In fact, this argument can be used constructionally from the degeneracies. From the notation of Theorem 1, the 2-fold degeneracies are seen to occur exactly when given an η, it turns out that $\eta' = -\eta$ also occurs (just at $\theta_0 = 0$ or π). Letting $\vec{c}_\eta$ be the corresponding eigenvector to C as in Theorem 1, now normalized, define $\sigma_\eta := \vec{c}_\eta \vec{c}_{-\eta}^{\,\dagger}$. Then, when $\theta_0 = 0$ or π, the idempotent

$$\mathsf{C}\sigma_\eta\mathsf{C} = (\mathsf{C}\vec{c}_\eta)(C^{-1}\vec{c}_{-\eta})^\dagger = \sigma_\eta.$$

Thus, with $\sigma := \sum_\eta \sigma_\eta$, one has $\mathsf{C}\sigma\mathsf{C} = \sigma$, from which along with $\sigma^2 = I$, one finds

$$\sigma\mathsf{C}\sigma = \mathsf{C}^{-1}.$$

Further, one then finds

$$\sigma A\sigma = \sigma(\mathsf{C} + \mathsf{C}^{-1})\sigma = \mathsf{C}^{-1} + \mathsf{C} = A,$$

so that A & σ commute (still exactly, when $\theta_0 = 0$ or π). Evidently (j,k)-th entry of σ is

$$\sigma_{jk} = \sum_\eta c_{\eta j} c^*_{-\eta k} = \frac{1}{n}\sum_\eta e^{i(\eta j - s_j)} e^{i(\eta k + s_k)}.$$

Then,

$$\sigma_{jk} = \frac{1}{n}\sum_l e^{i\left(\frac{\theta_0}{n} + 2\pi\frac{l}{n}\right)(j+k) + i(s_k - s_j)} = \delta_{(j+k),n} e^{i(\theta_0 + s_k - s_j)}. \qquad \square$$

Basically, with only the pure rotational symmetries, the numerous double degeneracies for the unphased case no longer occur.

4 Total energies

We focus on the chemical energies, $\varepsilon_0(G)$ & $\varepsilon_{\rm opt}(G)$.

Theorem 4 *Total chemical energies* $\varepsilon_0(C_n)$ *of a cycle* C_n *as function of* n & $\theta_0 \in [0,\pi]$ *are:*

$$\varepsilon_0(C_n) = \begin{cases} 4\cos\left(\frac{\theta_0-\pi}{n}\right) / \sin\left(\frac{\pi}{n}\right), & n = 4m; \\ 4\cos\left(\frac{\theta_0}{n}\right) / \sin\left(\frac{\pi}{n}\right), & n = 4m+2 \geq 6; \\ 4\cos\left(\frac{\theta_0-\pi/2}{n}\right)\cos^2\left(\frac{\pi}{2n}\right) / \sin\left(\frac{\pi}{n}\right), & n = 4m \pm 1. \end{cases}$$

The $\varepsilon_0(C_n)$ *at* $-\theta_0$ *are the same as at* $+\theta_0$ *and as at* $\theta_0 + 2\pi$.

Proof From Corollary 1.1, the eigenvalues are seen to change continuously as a function of θ_0, with the overall eigenspectrum invariant under $\theta_0 \to \theta_0 \pm 2\pi k$ and $\theta_0 \to \pm\theta_0$. Sets of these eigenvalues with a given occupation number do not change so long as θ_0 is retained in a suitable range. Indeed, we may choose such a suitable range to be $[0, \pi/n]$, which is half the range whereafter the eigenspectrum "rotates" ("reflects") back into itself. For $n = 4s$ or $4s + 2$, the graph is bipartite, and the unphased eigenvalues are symmetrically distributed about 0, with the case $4s + 2$ having no eigenvalues $= 0$, while $4s$ has a pair $= 0$. For the case $n = 4s + 2$, we then have $\varepsilon_0(G) = \sum_j 2 \cdot 2\cos(\theta_0 + 2\pi j/n)$, whence the sum is over the eigenvalues with an occupation number $= 2$, namely over $j = -s$ to $+s$. As such, we obtain

$$\begin{aligned} \varepsilon_0(C_{4s+2}) &= 2\sum_{k=-s}^{+s} 2\cos\left(\frac{\theta_0 + 2\pi k}{n}\right) = 2\Re\left(e^{i\theta_0/n}\sum_{k=-s}^{+s} e^{2\pi ki/n}\right) \\ &= 2\Re\left(e^{i\theta_0/n}\frac{e^{2\pi i(s+1)/n} - e^{-2\pi si/n}}{e^{2\pi i/n} - 1}\right) \\ &= \frac{2}{\sin(\pi/n)}\left[e^{i\theta_0/n} + e^{-i\theta/n}\right] = \frac{4\cos(\theta_0/n)}{\sin(\pi/n)}, \end{aligned}$$

where $\Re(\xi)$ indicates the real part of ξ.
Next, for $n = 4s$, we take eigenstates $j = -\frac{n}{4} \to +\frac{n}{4} + 1$ to have occupation numbers 2, and all others $= 0$. Thence, we have

$$\begin{aligned} \varepsilon_0(C_{4s}) &= 2\sum_{k=-s}^{s-1} 2\cos\left(\frac{\theta_0 + 2\pi k}{n}\right) = 2\Re\left(e^{i\theta_0/n}\sum_{k=-s}^{s-1} e^{2\pi ki/n}\right) \\ &= 2\Re\left(e^{i\theta_0/n}\frac{e^{2\pi si/n} - e^{-2\pi si/n}}{e^{2\pi i/n} - 1}\right) = \frac{4}{\sin(\pi/n)}\cos\left(\frac{\theta_0 - \pi}{n}\right). \end{aligned}$$

In a similar way, for $n = 4s + 1$, we obtain

$$\begin{aligned} \varepsilon_0(C_{4s+1}) &= 2\left[\sum_{k=-s}^{+s-1} 2\cos\left(\frac{\theta_0 + 2\pi k}{n}\right)\right] + 1 \cdot 2\cos\left(\frac{\theta_0 + 2\pi s}{n}\right) \\ &= 2\Re\left[e^{i\theta_0/n}\left(\sum_{k=-s}^{s-1} e^{2\pi ik/n} + \frac{1}{2}e^{2\pi is/n}\right)\right] \end{aligned}$$

$$
\begin{aligned}
&= 2\Re\left[e^{i\theta_0/n}\left(\frac{e^{2\pi is/n}-e^{-2\pi is/n}}{e^{2\pi i/n}-1}+\frac{1}{2}ie^{\pi i\left(\frac{1}{2}-\frac{1}{2n}\right)}\right)\right]\\
&= 2\Re\left[e^{i\theta_0/n}\left(\frac{ie^{3\pi i/2n}-(-i)e^{-\pi i/2n}}{2i\sin(\pi/n)}+\frac{1}{2}ie^{-\pi i/2n}\right)\right]\\
&= 2\Re\left[e^{i\theta_0/n}\left(\frac{e^{-\pi i/n}\cos(\pi/2n)}{\sin(\pi/n)}+ie^{-\pi i/2n}\frac{\cos(\pi/2n)\sin(\pi/2n)}{\sin(\pi/n)}\right)\right]\\
&= 2\,\frac{\cos(\pi/2n)}{\sin(\pi/n)}\Re\left[\left(e^{i(\theta_0-\pi/2)/n}+i\sin(\pi/2n)\right)e^{-i\pi/2n}\right)\Big]\\
&= 4\,\frac{\cos(\pi/2n)}{\sin(\pi/n)}\cos\left(\frac{\theta_0-\pi}{n}\right)-2\sin\left(\frac{\theta_0-\pi/2}{n}\right)\\
&= 2\cdot 4\cos^2\left(\frac{\pi}{2n}\right)\cos\left(\frac{\theta_0-\pi/2}{n}\right)\Big/\sin\left(\frac{\pi}{n}\right).
\end{aligned}
$$

Lastly, for $n = 4s - 1$, we obtain

$$
\begin{aligned}
\varepsilon_0(C_{4s-1}) &= 2\left[\sum_{k=1-s}^{+s-1} 2\cos\left(\frac{\theta_0+2\pi k}{n}\right)\right]+1\cdot 2\cos\left(\frac{\theta_0-2\pi s}{n}\right)\\
&= 2\Re\left[e^{i\theta_0/n}\left(\sum_{k=1-s}^{s-1} e^{2\pi ik/n}+\frac{1}{2}e^{-2\pi is/n}\right)\right]\\
&= 2\Re\left[e^{i\theta_0/n}\left(\frac{e^{2\pi is/n}-e^{-2\pi i(s-1)/n}}{e^{2\pi i/n}-1}+\frac{1}{2}(-i)e^{\pi i/2n}\right)\right]\\
&= 2\Re\left[e^{i\theta_0/n}\left(\frac{ie^{-\pi i/2n}-(-i)e^{+\pi i/2n}}{2i\sin(\pi/n)}-\frac{i}{2}e^{\pi i/2n}\right)\right]\\
&= 4\,\frac{\cos(\pi/2n)}{\sin(\pi/n)}\cos\left(\frac{\theta_0}{n}\right)+2\sin\left(\frac{\theta_0-\pi/2}{n}\right)\\
&= 2\cdot 4\cos^2\left(\frac{\pi}{2n}\right)\cos\left(\frac{\theta_0-\pi/2}{n}\right)/\sin\left(\frac{\pi}{n}\right).
\end{aligned}
$$

Hence, we arrive at the overall proof. □

These results are *size extensive* in that, for large n, the $\varepsilon_0(C_n)$ each scale $\sim n$. Indeed, the leading asymptotic term is identical in each case ($= 4n/\pi$), but has different lower order corrections $\sim 1/n$. Using (Maple-assisted) well-behaved Taylor series expansions, we have

Corollary 4.1 *The asymptotic large-n form for these $\varepsilon_0(C_n)$ are (for $\theta_0 \in [0, \pi]$):*

$$\varepsilon_0(C_n) - \frac{4n}{\pi} \asymp \begin{cases} 2\pi\left[\left(\frac{\theta_0}{\pi}-1\right)^2-\frac{1}{3}\right]\frac{1}{n}+O(n^{-3}), & n=4m \\ \pi\left[\left(\frac{\theta_0}{\pi}\right)^2-\frac{1}{3}\right]\frac{1}{n}+O(n^{-3}), & n=4m+2 \\ \pi\left[2\left(\frac{\theta_0}{\pi}-\frac{1}{2}\right)^2+\frac{1}{3}\right]\frac{1}{n}+O(n^{-3}), & n \text{ is odd.} \end{cases}$$

In addition to $\varepsilon_0(C_n)$, one may also address the fully maximized energy $\varepsilon_{opt}(G)$:

Theorem 5 *When n is even, the phased graph C_n has $\varepsilon_{opt} = \varepsilon_0$ (&$q_{opt} = 0$) regardless of θ_0. When n is odd (with $|\theta_0| \le \pi$)*

$$\varepsilon_{opt} = \varepsilon_0 + 2\sin\left|\frac{\frac{\pi}{2}-|\theta_0|}{n}\right| \quad and \quad q_{opt} = \begin{cases} \left.\begin{matrix} -1, & |\theta_0| < \frac{\pi}{2} \\ +1, & |\theta_0| > \frac{\pi}{2} \end{matrix}\right\}, & n=4m+1; \\ \left.\begin{matrix} -1, & |\theta_0| < \frac{\pi}{2} \\ +1, & |\theta_0| > \frac{\pi}{2} \end{matrix}\right\}, & n=4m-1. \end{cases}$$

A charge $q_{opt} = 0$ occurs for odd n at the boundaries when $\theta_0 = \pm\pi/2$.

Proof The problem is to determine which eigenvalues λ_j are positive for given n as θ ranges over representative values, say, from $-\pi/2$ to $+\pi/2$. The number $\#_+$ of such $\lambda > 0$ will be fixed over continuous ranges of θ_0, and the secondary problem of determining the number $\#_0$ of $\lambda = 0$ is answered as happening at the boundaries of θ_0 ranges where $\#_+$ changes. The $\#_0 > 0$ boundary points for θ_0 are conventionally identified by considering the condition under which an eigenvalue $\lambda_j = 0$, which occurs when $2\cos\frac{\theta_0+2\pi j}{n} = 0$. If we deal with angles in changes symmetric about 0, then we let $-n/2 \le j \le n/2$ and $-\pi \le \theta_0 \le +\pi$, so the $\lambda = 0$ condition occurs when $\frac{\theta_0+2\pi j}{n} = \pm\frac{\pi}{2}$ as is equivalent to $\theta_0 = 2\pi(-j \pm n/4)$. That is, to obtain θ_0 (such that $\lambda_j = 0$) for $-\pi < \theta_0 < \pi$, one needs j to be near $n/4$ – namely, $j = \mp\lfloor n/4\rfloor$ or $j = \mp\lceil n/4\rceil$. It thus becomes convenient to consider different cases depending on how close n comes to being divisible by 4.

For $n = 4m$, the situation is particularly simple, as then the θ_0 value giving $\lambda_j = 0$ (and $\#_0 > 0$) is just $\theta_0 = 0$, whence $j = \pm m$ and $\#_0 = 2$ & $\#_+ = \frac{n}{2} - 1$. For values of θ_0 with $0 < \theta_0 < \pi$, $\#_0 = 0$ & $\#_+ = n/2$. Thence, for all values of θ_0, $q_{opt} = 0$ & $\varepsilon_{opt} = \varepsilon_0$.

For $n = 4m + 2$, the θ_0 values giving $\lambda_j = 0$ (and $\#_0 > 0$) occur when $j = \pm m$, which in turn gives $\theta_0 = \pm\pi$. Again we obtain $q_{opt} = 0$ & $\varepsilon_{opt} = \varepsilon_0$ for all values of θ_0.

For $n = 4m+1$, the θ_0 values giving $\#_0 > 0$ occur when $j = \pm m$ and $\theta_0 = \mp\pi/2$. Then, for $-\pi/2 < \theta_0 < +\pi/2$, $\#_+ = m + 1$, $q_{opt} = +1$, and $\varepsilon_{opt} = \varepsilon_0 + \lambda_{\pm(m+1)}$. For $\theta_0 > \pi/2$ or $\theta_0 < -\pi/2$, we have $\#_+ = m$, $q_{opt} = -1$, and $\varepsilon_{opt} = \varepsilon_0 - \lambda_{\pm m}$.

For $n = 4m - 1$, the θ_0 values giving $\#_0 = \mp\pi/2$ occur when $j = \mp m$ and $\theta_0 = \mp\pi/2$. For $-\pi/2 < \theta_0 < \pi/2$, $\#_+ = m$, $q_{opt} = -1$, and $\varepsilon_{opt} = \varepsilon_0 + \lambda_{\pm m}$. For $\theta_0 > \pi/2$ or $\theta_0 < -\pi/2$, $\#_+ = m - 1$, $q_{opt} = +1$, and $\varepsilon_{opt} = \varepsilon_0 - \lambda_{\pm(m-1)}$.

The even-n result of the theorem is established with the first & second of these cases. Each of the odd-n cases breaks up into 2 subcases where the correction of

ε_{opt} to ε_0 involves an eigenvalue λ_j which is given in Theorems 1 and 2, but the cosine corresponding to λ_j has an argument near $\frac{\pi}{2}$, so that it is illuminating to rewrite $\cos\left(\frac{\pi}{2}-\delta\right)$ as $\pm\sin\delta = \sin|\delta|$. Here, $\delta = \pm\left(\frac{\frac{\pi}{2}-|\theta_0|}{n}\right)$ when n is odd. □

These energies also have the same leading asymptotic for as one another, and ε_0. We find

Corollary 5.1 *The asymptotic large-n form for these $\varepsilon_{opt}(C_n)$ are (for odd n):*

$$\varepsilon_{opt} - \frac{4n}{\pi} \asymp 2\pi\left[\left(\frac{\theta_0}{\pi}-\frac{1}{2}\right)^2 + \frac{1}{6} + \left|\frac{\pi}{2} - |\theta_0|\right|\right]\frac{1}{n} + O(n^{-3}), \quad n \text{ is odd.}$$

Another total energy $\varepsilon_{\text{math}}(G)$ is the sum of absolute values of eigenvalues of $A(G)$ [8–10]. It turns out that $\varepsilon_{\text{math}}(C_n) = \varepsilon_{opt}(C_n)$, but this is a special case of a much more general result, as proven in [1].

5 Comments relating to Aihara's resonance energy

Aihara suggested [11–14] a *topological resonance energy* (TRE) based on taking a difference of $\varepsilon_0(G)$ from a suitable *reference* energy $\varepsilon_{\text{ref}}(G)$. This $\varepsilon_{\text{ref}}(G)$ is a sum over the largest roots of a "circuitless" polynomial $\alpha(G;x)$ with occupation numbers for corresponding roots exactly matching those for $\varepsilon_0(G)$. This $\alpha(G;x)$ is taken to be the so-called *matching* polynomial [15] which involves summation over contributions from permutations as for the characteristic polynomial, but excluding cycles (other than 1- and 2-cycles). That is,

$$\text{TRE}(G) := \sum_k n_k[\lambda_k(G) - \mu_k(G)], \tag{2}$$

where the n_k are orbital occupation numbers, the $\lambda_k(G;x)$ are the adjacency-matrix eigenvalues, and the $\mu_k(G)$ are (the ordered) roots to

$$\alpha(G;x) := \sum_{\pi}^{G} (-1)^{n_2(P)} x^{n_1(P)}, \tag{3}$$

where the sum is over permutations P consisting solely of 1- and 2-cycles on edges of G, and $n_c(P)$ denotes the number of c-cycles in P. The usual characteristic polynomial is

$$\phi(G;x) := \det(xI - A) = \sum_{P\in S_n} (-1)^{n+n_e(\pi)} \left[\prod_{j}^{j\neq\pi j} a_{j,Pj}\right] x^{n_1(P)}, \tag{4}$$

where I is a unit diagonal matrix, the sum is over all permutations P of the symmetric group S_n, Pj is the image of j under P, $a_{j,k}$ is the (j,k)-th (phased) entry of A, and $n_e(P)$ is the number of even cycles in P.

Lemma 6 *For a phased cycle C_n,*

$$\phi(C_n; x) = \alpha(C_n; x) - 2\cos\theta_0. \tag{5}$$

Proof By definitions (3) and (4), the expansion of $\phi(C_n; x)$ in powers of x entirely includes a similar expansion of $\alpha(C_n; x)$ and one additional term corresponding to the weight for the cyclic permutation of C_n. Of course, the cycling permutation may go in either direction around the graph cycle, whence their net weight in the brackets in (4) is

$$\prod_{j=1}^{n} a_{j,j+1} + \prod_{j=1}^{n} a_{j+1,j} = \prod_{j=1}^{n} e^{i\theta_{j,j+1}} + \prod_{j=1}^{n} e^{-i\theta_{j,j+1}} = e^{i\theta_0} + e^{-i\theta_0} = 2\cos\theta_0.$$

The sign with which this weight is included in (5) is $(-1)^n \times (-1)^{n+n_e(\pi)} = -1$. □

Here, we note that the sign for $2\cos\theta_0$ exactly obeys the famous Sachs method [16], in which undirected cycles of all lengths invariably have the same weight -2 in the expansion of the characteristic polynomial $\phi(C_n; x) := \det(xI - A)$.

Aihara's resonance energy was defined with respect to a reference polynomial, but in general a reference system might be desired. Our Lemma 6 accords with Aihara's observation [19] that at least for a single cycle we have a reference system (at $\theta_0 = \pi/2$).

6 Conclusion

The circumstance of a phased cycle graph is here fairly thoroughly treated. The eigenproblem is solved, symmetries are identified, various net energies are developed, and a reference system for Aihara's topological resonance energy is noted. The eigenspectrum for the phased case is evidently intimately related to that of the unphased case, as is pictorially evident from Corollary 1.1 generalizing the Frost-Musulin [5] diagrammatics. The cyclic part of the symmetry of the unphased cycle is preserved regardless of the pattern of phasing, and the involutory symmetries are typically absent. A reference system for Aihara's topological resonance energy has been identified in the cyclic case.

Notably, the so-called "extended" Hückel-Möbius rule (eg., as advocated by Zimmermann [17,18]) accounting for the consequences of the "Möbius" sign effect is now even further extended to deal with general net phases. When the numbers of sites & electrons match: If the net phase $\theta_0 = 0, n = 4m + 2$ is favored, then, if $\theta = \pi$, then $n = 4m$ is favored; and if intermediate phasing with $\theta_0 = \pi/2$, occurs, then $n = 4m \pm 1$ is favored. Net π-network charges q_{opt} other than 0, are favored for odd n, in accordance with Theorem 5.

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References

1. D.J. Klein, V.R. Rosenfeld, Phased graphs and graph energies. J. Math. Chem., accepted
2. P.J. Davis, *Circulant Matrices* (Wiley, New York, 1971)
3. E. Hückel, Quantentheoretische Beiträge zum Benzolproblem. III, Quantentheoretische Beiträge zum problem der aromatschen ungesättigten verbindungen. Zeit. für Physik. **76**, 628–648 (1932)
4. E. Heilbronner, Hückel molecular orbitals of Möbius-type conformations of annulenes. Tetrahedron Lett. **29**, 1923–1928 (1964)
5. A.A. Frost, B.J. Musulin, Mnemonic device for molecular-orbital energies. J. Chem. Phys. **21**, 572–573 (1953)
6. H.E. Zimmermann, On molecular orbital correlation diagrams, the occurrence of Möbius systems in cyclization reactions, and factors controlling ground and excited state reactions. I. J. Am. Chem. Soc. **88**, 1564–1565 (1966)
7. M. Hamermesh, *Group Theory and its Application to Physical problems*, Addison-Wesley, Reading, Massachusetts, 1962, 1964; Dover, New York (1989)
8. I. Gutman, The energy of a graph. Ber. Math.-Stat. Sekt. Forschungszent. Graz **103**, 1–22 (1978)
9. S.-L. Lee, R.R. Lucchese, S.Y. Chu, Topological analysis of eigenvectors of the adjacent matrices in graph theory: the concept of internal connectivity. Chem. Phys. Lett. **137**, 279–284 (1987)
10. S.-L. Lee, R.R. Lucchese, S.Y. Chu, Net signs and eigenvalues of molecular graphs: some analogies. Chem. Phys. Lett. **191**, 87–91 (1992)
11. J. Aihara, Topological resonance energy, bond resonance energy, and circuit resonance energy. J. Am. Chem. Soc. **98**, 2750–2758 (1976)
12. J. Aihara, J. Org. Chem. **41**, 2488–2490 (1976)
13. J. Aihara, J. Am. Chem. Soc. **99**, 2048 (1977)
14. J. Aihara, Bull. Chem. Soc. Japan **50**, 2010 (1977)
15. I. Gutman, N. Trinajstić, Graph theory and molecular orbitals, XIV. On topological definition of resonance energy. Acta Chimica Acad. Sci. Hung. **91**, 203–209 (1976)
16. D.M. Cvetković, M. Doob, H. Sachs, *Spectra of Graphs: Theory and Application* (Academic Press, New York, 1980)
17. H.E. Zimmermann, The Möbius-Hückel concept in organic chemistry, application to organic molecules and reactions. Acc. Chem. Res. **4**, 272–280 (1971)
18. H.E. Zimmermann, *Quantum Mechanics for Organic Chemists* (Academic Press, New York, 1975)
19. J. Aihara, Matrix representation of an olefinic reference structure for monocyclic conjugated hydrocarbons. Bull. Chem. Soc. Japan **52**, 1529–1530 (1972)