MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **97** (2027) 561–588
ISSN: 0340–6253
doi: 10.46793/match.97-2.15326

A Resonance-Weighted Kirchhoff Index Based on Pauling Bond Orders of Kekuléan Molecular Graphs

Qamar Din[a,*]

[a] *Department of Mathematics, University of Poonch Rawalakot, Azad Jammu & Kashmir, Pakistan*

qamar.sms@gmail.com

(Received April 26, 2026)

Abstract

We study a resistance-distance invariant for Kekuléan molecular graphs obtained by assigning to each edge its Pauling bond order as an electrical conductance. The associated Pauling-weighted electrical network has finite pairwise effective resistances exactly when the positive bond-order support is connected, and in this case the corresponding resonance-weighted Kirchhoff index is well defined. The construction is a specialization of the weighted Kirchhoff index, but the weights are not external parameters: they are the edge frequencies in the Kekulé ensemble. Equivalently, the weighted Laplacian is the average of the Laplacians of all Kekulé structures. We prove trace normalization, a connected-support criterion, comparison inequalities, a conductance sensitivity formula, and the exact scaling law in the uniform bond-order case. In particular, uniform Pauling bond order recovers the ordinary Kirchhoff index only when the common order is one. Exact benchmark computations and bond-order profiles are given for benzene, naphthalene, anthracene, and phenanthrene. For the full linear-acene family we derive an exact finite-sum formula and the leading cubic growth of the resonance-weighted Kirchhoff index; these results provide reference values for a carefully stated catacondensed-benzenoid extremal problem.

*Corresponding author.

This work is licensed under a Creative Commons "Attribution 4.0 International" license.

1 Introduction

The Kirchhoff index is one of the most useful resistance-distance invariants in chemical graph theory. If every edge of a connected graph is treated as a unit resistor, the resistance distance between two vertices is the corresponding effective electrical resistance, and the Kirchhoff index is the sum of these resistances over all unordered vertex pairs. Since its introduction by Klein and Randić and the subsequent observation that it coincides with the quasi-Wiener index associated with Wiener-type distance descriptors, the invariant has become a standard spectral and electrical descriptor of molecular graphs [6, 8, 16]. Resistance distance and Kirchhoff-type quantities also have a well-developed weighted-graph version, in which positive conductances are assigned to the edges [1]. Exact and extremal Kirchhoff-index formulae for unweighted hexagonal chains are also known, including results for linear chains and extremal hexagonal chains [7, 17–19].

For conjugated hydrocarbons, the assumption that all bonds contribute equal conductance is chemically restrictive. A Kekuléan molecular graph has a family of Kekulé structures, or perfect matchings, and an edge may occur in many, few, or all of them. The Pauling bond order of an edge is the fraction of Kekulé structures in which the edge is selected [5, 13, 14]. Bond-order weighted molecular graphs have appeared previously as structure–property descriptors [4, 9]; nevertheless, using the Pauling frequencies themselves as electrical conductances leads to a different resistance-distance invariant. In particular, the present construction is not obtained by assigning an arbitrary empirical weight to each bond; the conductance vector is forced by the perfect-matching ensemble and is therefore tied to the resonance structure of the graph. Although the limitations of Pauling bond orders as chemical bond-order descriptors are known [15], the quantity remains a natural combinatorial measure of how the Kekulé ensemble distributes double-bond character over the graph. It is therefore meaningful to ask what resistance-distance theory becomes when the unit conductance of each bond is replaced by its Pauling bond order.

This paper develops this chemically constrained specialization of the

weighted Kirchhoff index. The general weighted-Laplacian framework is not new; the point here is that the conductances are fixed internally by the Kekulé ensemble rather than chosen as external edge parameters. Given a connected graph with at least one perfect matching, let p_e be the Pauling bond order of the edge e. We form the weighted Laplacian L_p with conductances p_e and define

$$\mathrm{RKf}_p(G) = n\ \mathrm{tr}(L_p^+),$$

provided the positive bond-order support is connected. Equivalently, $\mathrm{RKf}_p(G)$ is the sum of all effective resistances in the network whose edge conductances are the Pauling bond orders. The construction is not proposed as a new general theory of weighted resistance distance; its novelty is the chemically determined choice of conductances and the resulting connection with the average of the Laplacians of the individual Kekulé structures.

The main purpose of this paper is to put this resonance-weighted invariant on a mathematically correct footing. In particular, equality cases require care. If all positive Pauling bond orders are equal to c and the positive support is H, then $L_p = cL(H)$ and hence

$$\mathrm{RKf}_p(G) = c^{-1}\,\mathrm{Kf}(H),$$

not $\mathrm{Kf}(H)$. Thus benzene, whose six edges all have Pauling bond order $1/2$, has resonance-weighted Kirchhoff index 35, whereas the ordinary Kirchhoff index of C_6 is $35/2$. This simple example rules out the common but incorrect expectation that uniform bond order should return the ordinary Kirchhoff index.

The contributions are as follows.

(i) A resonance-weighted Laplacian and the corresponding Kirchhoff index are defined for graphs with connected positive bond-order support, and this support condition is shown to be exactly the condition for finite all-pairs Pauling-weighted effective resistance.

(ii) The invariant is identified with the Kirchhoff index of the average Lapla-

cian of all Kekulé structures.

(iii) Support-dependent comparison inequalities are proved in terms of the smallest and largest positive Pauling bond orders, with careful equality statements.

(iv) A conductance sensitivity formula is derived for the weighted network obtained after the Pauling weights have been fixed.

(v) Exact benchmark values are computed for benzene, naphthalene, anthracene, and phenanthrene. In addition, a closed finite-sum formula and a leading-order asymptotic estimate are proved for the whole linear-acene family.

(vi) The resulting exact linear-acene values are used to formulate a cautious extremal problem for catacondensed benzenoids.

The concluding section records the resulting extremal questions as open problems, since the currently available computations do not yet determine a complete extremal theory.

2 Preliminaries

All graphs considered here are finite, simple, undirected, and connected unless stated otherwise; standard terminology follows [2]. Let $G = (V, E)$, where $|V| = n$ and $|E| = m$. The degree of v is denoted by d_v. The ordinary Laplacian is $L = D - A$. The spectral facts used below are standard for graph Laplacians [3, 11, 12]. Its eigenvalues are

$$0 = \mu_1 < \mu_2 \leq \cdots \leq \mu_n$$

when G is connected. The Moore–Penrose inverse of L is denoted by L^+. The resistance distance between u and v is

$$\Omega_G(u, v) = (\mathbf{e}_u - \mathbf{e}_v)^T L^+ (\mathbf{e}_u - \mathbf{e}_v),$$

and the Kirchhoff index is

$$\mathrm{Kf}(G) = \sum_{\{u,v\}\subseteq V} \Omega_G(u,v) = n\ \mathrm{tr}(L^+) = n\sum_{i=2}^{n} \frac{1}{\mu_i}.$$

A perfect matching of G is a set $M \subseteq E$ such that every vertex of G is incident with exactly one edge of M; see [10] for the general matching-theoretic background. The set of perfect matchings is denoted by $\mathcal{M}(G)$, and

$$\kappa(G) = |\mathcal{M}(G)|$$

is the Kekulé count. In molecular terminology, a perfect matching of a benzenoid or alternant hydrocarbon graph is a Kekulé structure.

Definition 1. Let G be a graph with $\kappa(G) > 0$. For $e \in E(G)$, the Pauling bond order of e is

$$p_e = \frac{|\{M \in \mathcal{M}(G) : e \in M\}|}{\kappa(G)}.$$

An edge is called allowed if $p_e > 0$, fixed if $p_e = 1$, and forbidden if $p_e = 0$.

The following elementary identity will be used repeatedly.

Lemma 1 (Perfect-matching sum rule)**.** *If $\kappa(G) > 0$, then*

$$\sum_{e\in E(G)} p_e = \frac{n}{2}.$$

Proof. Every perfect matching contains exactly $n/2$ edges. Hence

$$\sum_{M\in\mathcal{M}(G)} |M| = \kappa(G)\frac{n}{2}.$$

On the other hand, counting the same incidences edge by edge gives

$$\sum_{M\in\mathcal{M}(G)} |M| = \sum_{e\in E(G)} |\{M \in \mathcal{M}(G) : e \in M\}| = \kappa(G) \sum_{e\in E(G)} p_e.$$

Division by $\kappa(G)$ gives the assertion. ∎

Definition 2. The positive bond-order support of G is

$$G_p = (V, E_p), \qquad E_p = \{e \in E : p_e > 0\}.$$

We say that G is resonance-connected if G_p is connected.

The resonance-connectedness assumption is not a cosmetic restriction. It is exactly the condition under which the Pauling-weighted electrical network has finite resistance between every pair of vertices.

Proposition 1 (Finiteness criterion)**.** *Let G be a graph with $\kappa(G) > 0$, and let L_p be the weighted Laplacian formed from the Pauling bond orders. Then*

$$\operatorname{rank} L_p = n - 1$$

if and only if G_p is connected. Equivalently, all pairwise Pauling-weighted effective resistances are finite if and only if G is resonance-connected.

Proof. For any $x \in \mathbb{R}^n$,

$$x^T L_p x = \sum_{uv \in E_p} p_{uv}(x_u - x_v)^2.$$

Since every coefficient in this sum is positive, the nullspace consists precisely of the vectors that are constant on each connected component of G_p. Thus the nullity of L_p is the number of connected components of G_p. Hence $\operatorname{rank} L_p = n - 1$ exactly when G_p is connected. The same condition is equivalent to finiteness of all effective resistances in the associated conductance network. ■

3 The resonance-weighted Kirchhoff index

Choose an arbitrary orientation of the edges and let B be the corresponding vertex-edge incidence matrix. Denote by β_e the incidence column associated with the oriented edge e. Let

$$P = \operatorname{diag}(p_e : e \in E).$$

The weighted Laplacian determined by the Pauling bond orders is

$$L_p = BPB^T = \sum_{e \in E} p_e \, \beta_e \beta_e^T .$$

Equivalently,

$$(L_p)_{uv} = \begin{cases} -p_{uv}, & uv \in E,\ u \neq v, \\ \sum\limits_{w \sim u} p_{uw}, & u = v, \\ 0, & \text{otherwise.} \end{cases}$$

Definition 3. Let G be a resonance-connected graph with $\kappa(G) > 0$. The resonance-weighted resistance distance is

$$\Omega_p(u, v) = (\mathbf{e}_u - \mathbf{e}_v)^T L_p^+ (\mathbf{e}_u - \mathbf{e}_v),$$

and the resonance-weighted Kirchhoff index is

$$\mathrm{RKf}_p(G) = \sum_{\{u,v\} \subseteq V} \Omega_p(u, v) = n \ \mathrm{tr}(L_p^+).$$

If $0 = \nu_1 < \nu_2 \leq \cdots \leq \nu_n$ are the eigenvalues of L_p, then

$$\mathrm{RKf}_p(G) = n \sum_{i=2}^{n} \frac{1}{\nu_i}.$$

The trace of L_p is fixed by the perfect-matching sum rule.

Proposition 2. *If G is a graph with $\kappa(G) > 0$, then*

$$\mathrm{tr}(L_p) = n.$$

If, in addition, G is resonance-connected and $0 = \nu_1 < \nu_2 \leq \cdots \leq \nu_n$ are the eigenvalues of L_p, then

$$\nu_2 + \cdots + \nu_n = n.$$

Proof. For a weighted Laplacian,

$$\operatorname{tr}(L_p) = \sum_{v \in V} \sum_{e \ni v} p_e = 2 \sum_{e \in E} p_e.$$

The result follows from Lemma 1. ■

Proposition 3 (Average-Kekulé Laplacian representation)**.** *For every perfect matching M, let L_M be the Laplacian of the graph (V, M). Then*

$$L_p = \frac{1}{\kappa(G)} \sum_{M \in \mathcal{M}(G)} L_M.$$

Proof. For an edge e, the coefficient of the elementary edge Laplacian $\beta_e \beta_e^T$ in the right-hand side is the fraction of perfect matchings containing e, namely p_e. This is exactly the coefficient of $\beta_e \beta_e^T$ in L_p. ■

Proposition 4 (Deletion formula for bond orders)**.** *Let $e = uv \in E(G)$. Then*

$$p_e = \frac{\kappa(G - u - v)}{\kappa(G)},$$

where $G - u - v$ is the graph obtained by deleting u, v, and all incident edges. We use the standard convention $\kappa(\varnothing) = 1$.

Proof. A perfect matching of G containing $e = uv$ is obtained uniquely by adding e to a perfect matching of $G - u - v$. Conversely, every perfect matching of $G - u - v$, together with e, gives a perfect matching of G containing e. Dividing the number of such matchings by $\kappa(G)$ gives the formula. ■

4 Comparison with the ordinary Kirchhoff index

The next theorem is the basic comparison principle for weighted resistance indices. It is stated in a form that will also be useful outside the Pauling-bond-order setting.

Theorem 5 (Monotonicity)**.** *Let $a = (a_e)$ and $b = (b_e)$ be two positive conductance systems on the same connected graph G, and let L_a, L_b be the corresponding weighted Laplacians. If*

$$0 < a_e \le b_e \qquad (e \in E),$$

then

$$n \operatorname{tr}(L_a^+) \ge n \operatorname{tr}(L_b^+).$$

If at least one inequality $a_e < b_e$ holds, then the inequality is strict.

Proof. Both Laplacians annihilate $\mathbf{1}$ and are positive definite on the subspace

$$\mathbf{1}^\perp = \{x \in \mathbb{R}^n : x^T \mathbf{1} = 0\}.$$

For $x \in \mathbf{1}^\perp$,

$$x^T (L_b - L_a) x = \sum_{e=uv \in E} (b_e - a_e)(x_u - x_v)^2 \ge 0.$$

Thus $L_a \preceq L_b$ on $\mathbf{1}^\perp$. Inversion reverses the Loewner order on positive definite matrices, and hence

$$L_b^{-1} \preceq L_a^{-1} \quad \text{on } \mathbf{1}^\perp.$$

Taking traces on $\mathbf{1}^\perp$ gives the asserted inequality.

For strictness, set $C = L_b - L_a$ and $L_t = L_a + tC$, $0 \le t \le 1$, again as operators on $\mathbf{1}^\perp$. If at least one conductance is increased, then $C \ne 0$. The function

$$\phi(t) = \operatorname{tr}(L_t^{-1})$$

satisfies

$$\phi'(t) = -\operatorname{tr}(L_t^{-1} C L_t^{-1}) = -\sum_{e=uv \in E} (b_e - a_e)\, \beta_e^T L_t^{-2} \beta_e.$$

At least one summand is strictly positive because $\beta_e \ne 0$ in $\mathbf{1}^\perp$ and L_t^{-2}

is positive definite there. Hence $\phi'(t) < 0$ for $0 \le t \le 1$, and therefore

$$\operatorname{tr}(L_a^{-1}) > \operatorname{tr}(L_b^{-1}).$$

This proves the strict inequality. ■

Corollary 6. *Let G be resonance-connected and let G_p be its positive bond-order support. Then*

$$\mathrm{RKf}_p(G) \ge \mathrm{Kf}(G_p) \ge \mathrm{Kf}(G).$$

In particular, for every resonance-connected graph with $n > 2$,

$$\mathrm{RKf}_p(G) > \mathrm{Kf}(G).$$

Proof. Apply Theorem 5 on the support graph G_p, with $a_e = p_e$ and $b_e = 1$. Since $0 < p_e \le 1$ on E_p, this gives $\mathrm{RKf}_p(G) \ge \mathrm{Kf}(G_p)$. The second inequality follows from Rayleigh monotonicity: adding the forbidden edges $E \setminus E_p$ with unit conductance cannot increase any effective resistance.

It remains only to justify strictness for $n > 2$. Equality in the first comparison would force $p_e = 1$ for every edge of E_p. Then Lemma 1 would give $|E_p| = n/2$. A connected graph on $n > 2$ vertices has at least $n - 1 > n/2$ edges, a contradiction. Hence $\mathrm{RKf}_p(G) > \mathrm{Kf}(G_p)$, and therefore $\mathrm{RKf}_p(G) > \mathrm{Kf}(G)$. ■

The next result gives the correct sharp form of the comparison with the ordinary Kirchhoff index.

Theorem 7 (Sharp comparison by extremal bond orders)**.** *Assume that G is resonance-connected and put*

$$p_{\min} = \min_{e \in E_p} p_e, \qquad p_{\max} = \max_{e \in E_p} p_e.$$

Then

$$\frac{1}{p_{\max}}\,\mathrm{Kf}(G_p) \le \mathrm{RKf}_p(G) \le \frac{1}{p_{\min}}\,\mathrm{Kf}(G_p).$$

The constants $p_{\min}^{-1}$ and $p_{\max}^{-1}$ are support-dependent and cannot be improved in general. If all positive bond orders are equal, then the two bounds coincide and equality holds.

Proof. On the support G_p,

$$p_{\min} L(G_p) \preceq L_p \preceq p_{\max} L(G_p)$$

as quadratic forms on $\mathbf{1}^{\perp}$. Applying Theorem 5 to $p_{\min} L(G_p) \preceq L_p$ gives

$$\mathrm{RKf}_p(G) \leq p_{\min}^{-1} \,\mathrm{Kf}(G_p),$$

and applying it to $L_p \preceq p_{\max} L(G_p)$ gives

$$p_{\max}^{-1} \,\mathrm{Kf}(G_p) \leq \mathrm{RKf}_p(G).$$

If $p_e = c$ for every $e \in E_p$, then $L_p = cL(G_p)$ and

$$\mathrm{RKf}_p(G) = c^{-1} \,\mathrm{Kf}(G_p).$$

Thus neither extremal constant can be decreased in a general statement depending only on $p_{\min}$, $p_{\max}$, and the support graph. ■

Corollary 8 (Uniform bond order)**.** *If the positive support is G itself and $p_e = c$ for all $e \in E(G)$, then*

$$\mathrm{RKf}_p(G) = \frac{1}{c} \,\mathrm{Kf}(G).$$

Since $\sum_e p_e = n/2$, the common value is $c = n/(2m)$, and hence

$$\mathrm{RKf}_p(G) = \frac{2m}{n} \,\mathrm{Kf}(G).$$

Remark. Corollary 8 is the corrected equality statement. Uniform Pauling bond order does not recover the ordinary Kirchhoff index, except in the degenerate case $c = 1$. In benzene, $c = 1/2$, so the resonance-weighted index is twice the ordinary Kirchhoff index.

Corollary 9 (Kekulé-count bounds)**.** *For every resonance-connected graph,*

$$p_{\min} \geq \frac{1}{\kappa(G)} \quad \textit{and hence} \quad \mathrm{RKf}_p(G) \leq \kappa(G)\ \mathrm{Kf}(G_p).$$

If no edge of G_p is fixed, then

$$p_{\max} \leq \frac{\kappa(G)-1}{\kappa(G)} \quad \textit{and hence} \quad \mathrm{RKf}_p(G) \geq \frac{\kappa(G)}{\kappa(G)-1}\ \mathrm{Kf}(G_p).$$

Proof. For each edge $e \in E_p$, the integer $|\{M : e \in M\}|$ is at least 1, so $p_e \geq 1/\kappa(G)$. If e is not fixed, then this integer is at most $\kappa(G)-1$, so $p_e \leq (\kappa(G)-1)/\kappa(G)$. The bounds follow from Theorem 7. ■

5 Trace and sensitivity bounds

The trace normalization in Proposition 2 yields a universal lower bound independent of the ordinary graph structure.

Theorem 10 (Universal trace lower bound)**.** *If G is resonance-connected, then*

$$\mathrm{RKf}_p(G) \geq (n-1)^2.$$

Proof. By Proposition 2,

$$\nu_2 + \cdots + \nu_n = n.$$

The harmonic-arithmetic mean inequality gives

$$\sum_{i=2}^{n} \frac{1}{\nu_i} \geq \frac{(n-1)^2}{\sum_{i=2}^{n} \nu_i} = \frac{(n-1)^2}{n}.$$

Multiplication by n proves the claim. ■

Remark (Equality in the universal lower bound). Equality in Theorem 10 holds if and only if

$$\nu_2 = \cdots = \nu_n = \frac{n}{n-1}.$$

Indeed, this is exactly the equality case in the harmonic-arithmetic mean inequality used above.

A second basic estimate uses the extremal positive eigenvalues.

Proposition 11. *Let $0 < \nu_2 \le \cdots \le \nu_n$ be the positive eigenvalues of L_p. Then*

$$\frac{n(n-1)}{\nu_n} \le \mathrm{RKf}_p(G) \le \frac{n(n-1)}{\nu_2}.$$

Proof. The assertion follows immediately from

$$\frac{1}{\nu_n} \le \frac{1}{\nu_i} \le \frac{1}{\nu_2}, \qquad i = 2, \dots, n. \qquad \blacksquare$$

The next formula gives a precise local sensitivity interpretation.

Theorem 12 (Conductance sensitivity)**.** *Let $c = (c_e)_{e \in E}$ be a positive conductance vector on a connected graph, and set*

$$F(c) = n \operatorname{tr}(L_c^+), \qquad L_c = \sum_{e \in E} c_e \, \beta_e \beta_e^T.$$

Then, for each edge e,

$$\frac{\partial F}{\partial c_e} = -\, n \, \beta_e^T (L_c^+)^2 \beta_e.$$

In particular, if all other conductances are held fixed, then F is strictly decreasing in each conductance coordinate c_e.

Proof. Restrict L_c to $\mathbf{1}^\perp$, where it is positive definite. On this subspace, the Moore–Penrose inverse is the ordinary inverse. Since

$$\frac{\partial L_c}{\partial c_e} = \beta_e \beta_e^T,$$

the derivative of the inverse gives

$$\frac{\partial}{\partial c_e} \operatorname{tr}(L_c^{-1}) = -\operatorname{tr}\big(L_c^{-1} \beta_e \beta_e^T L_c^{-1}\big) = -\beta_e^T L_c^{-2} \beta_e.$$

Returning to Moore–Penrose notation gives the displayed expression. The vector β_e lies in $\mathbf{1}^\perp$ and is nonzero. Since L_c^+ is positive definite on $\mathbf{1}^\perp$, the quadratic form is positive. Hence the derivative is negative. $\blacksquare$

Remark. For Pauling bond orders, the coordinates p_e are constrained by the perfect-matching ensemble and by Lemma 1. Theorem 12 should therefore be read as a formal conductance sensitivity statement, not as a claim that a single Pauling bond order can always be varied independently within the class of molecular graphs.

6 Exact benchmark computations

The following examples are included both as checks on the theory and as benchmark values for future work. The Pauling bond orders were obtained from Proposition 4, or equivalently by enumerating the perfect matchings for these small benzenoids, and the resistance sums were computed from rational weighted Laplacians. The computational convention is the following: after the labelled weighted Laplacian L_p is formed, the identity

$$L_p^+ = \left(L_p + \frac{1}{n}J\right)^{-1} - \frac{1}{n}J, \qquad J = \mathbf{1}\mathbf{1}^T,$$

is used to evaluate $n\,\mathrm{tr}(L_p^+)$ by exact rational arithmetic. Thus all entries below can be reproduced from the displayed edge weights without numerical optimization or floating-point inversion. This procedure also checks that the positive bond-order support is connected in each benchmark. A minimal reproducibility protocol is: enumerate or otherwise determine the Pauling orders p_e, assemble the rational weighted Laplacian L_p, form $L_p + n^{-1}J$, invert this nonsingular rational matrix, subtract $n^{-1}J$, and finally compute $n\,\mathrm{tr}(L_p^+)$.

Example 1 (Benzene)**.** For benzene C_6, there are two Kekulé structures and every edge occurs in one of them. Therefore $p_e = 1/2$ for all six edges. Since

$$\mathrm{Kf}(C_6) = \frac{6^3 - 6}{12} = \frac{35}{2},$$

Corollary 8 gives

$$\mathrm{RKf}_p(C_6) = 2\,\mathrm{Kf}(C_6) = 35.$$

Table 1. Exact resonance-weighted Kirchhoff indices for small benzenoid graphs.

Graph	n	m	κ	$\mathrm{Kf}(G)$	$\mathrm{RKf}_p(G)$
Benzene	6	6	2	35/2	35
Naphthalene	10	11	3	465/7	659/4
Anthracene	14	16	4	33425/204	2243/5
Phenanthrene	14	16	5	8200/51	12057/26

Table 2 records the positive Pauling bond-order profiles used in the weighted computations. In the profile column, the superscript gives the number of edges with the indicated bond order.

Table 2. Positive Pauling bond-order profiles for the benchmark benzenoids.

Graph	$p_{\min}$	$p_{\max}$	Profile on E_p
Benzene	1/2	1/2	$(1/2)^6$
Naphthalene	1/3	2/3	$(1/3)^7, (2/3)^4$
Anthracene	1/4	3/4	$(1/4)^8, (1/2)^4, (3/4)^4$
Phenanthrene	1/5	4/5	$(1/5)^3, (2/5)^8, (3/5)^4, (4/5)^1$

For reproducibility, the placement of the bond orders is as follows. Benzene is the cycle C_6. Naphthalene and anthracene use the linear-acene labelling in Theorem 13 with $h = 2$ and $h = 3$, respectively; the convention is illustrated in Figure 1. For phenanthrene we use the labelled graph in Figure 2, whose vertices are $w_1, \ldots, w_{14}$ and whose weighted edges are listed in Table 3; an edge in the row $q/5$ has Pauling bond order $q/5$. These labelled edge data determine the corresponding rational Laplacian uniquely.

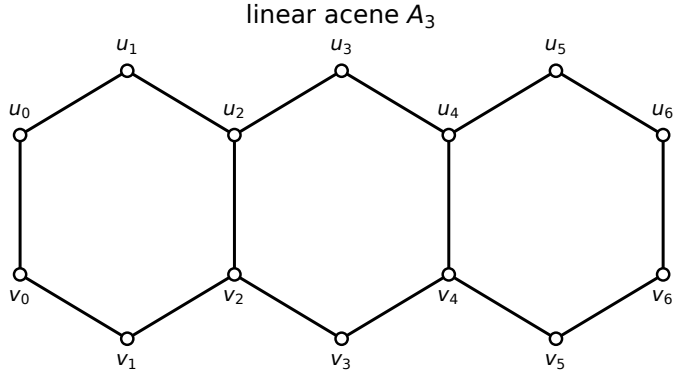

Figure 1. Labelling convention for the linear acene A_h, illustrated for $h = 3$. In general the upper and lower rows are $u_0, \ldots, u_{2h}$ and $v_0, \ldots, v_{2h}$, with vertical fusion edges at the even positions.

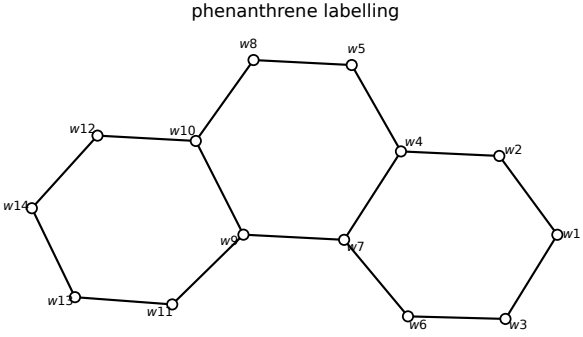

Figure 2. Labelled phenanthrene graph used in Table 3. The Pauling bond orders are listed separately in the table.

Table 3. Labelled Pauling-weighted edge data used for phenanthrene.

Bond order	Edges
1/5	$w_{10}w_8$, w_4w_5, w_7w_9
2/5	$w_{10}w_{12}$, $w_{11}w_9$, $w_{13}w_{14}$, w_2w_4, w_3w_1, w_6w_7, w_7w_4, w_9w_{10}
3/5	$w_{11}w_{13}$, $w_{14}w_{12}$, w_1w_2, w_3w_6
4/5	w_5w_8

The table shows two important features. First, $\mathrm{RKf}_p(G)$ is substantially larger than $\mathrm{Kf}(G)$, as predicted by Corollary 6. Second, RKf_p distinguishes anthracene and phenanthrene more strongly than the ordinary Kirchhoff index: the ordinary values are close, whereas the Pauling-weighted values differ by about 15.13. This is consistent with the fact that angular fusion changes the distribution of Kekulé bond orders.

For linear acenes A_h, where h is the number of fused hexagons, the Kekulé count is $h+1$. Numerical benchmark values for the first members are listed in Table 4. The entries for $h = 1, 2, 3$ agree with the exact values in Table 1; the remaining entries are evaluations of the closed formula in Theorem 13.

Table 4. Numerical benchmark values for the linear acenes A_h.

h	n	m	$\kappa(A_h)$	$\mathrm{RKf}_p(A_h)$
1	6	6	2	35.0000
2	10	11	3	164.7500
3	14	16	4	448.6000
4	18	21	5	943.3750
5	22	26	6	1704.8869
6	26	31	7	2788.2146
7	30	36	8	4247.8760
8	34	41	9	6137.9426

Lemma 2 (Spectrum of the acene coupling matrix)**.** *Let X_h be the $(h+1)\times h$ bidiagonal matrix defined by*

$$(X_h)_{j,j} = h - j, \qquad (X_h)_{j+1,j} = j + 1, \qquad 0 \le j \le h-1, \tag{1}$$

all other entries being zero. Then

$$\det(zI_h - X_h^T X_h) = \prod_{k=1}^{h} \big(z - k(2h+1-k)\big). \tag{2}$$

Consequently, the eigenvalues of $X_h^T X_h$ *are* $k(2h+1-k)$, $1 \le k \le h$.

Proof. Put $A_h = X_h^T X_h$ and index rows and columns by $j = 0, 1, \dots, h-1$. A direct multiplication gives

$$(A_h)_{j,j} = (h-j)^2 + (j+1)^2, \qquad (A_h)_{j,j+1} = (j+1)(h-j-1), \tag{3}$$

with the symmetric lower off-diagonal entries. Thus, for a vector written as $f = (f(0), \dots, f(h-1))^T$,

$$\begin{aligned} (A_h f)(j) = {} & j(h-j) f(j-1) + \big((h-j)^2 + (j+1)^2\big) f(j) \\ & + (j+1)(h-j-1) f(j+1), \qquad 0 \le j \le h-1, \end{aligned} \tag{4}$$

where the first term is absent at $j = 0$ and the last term is absent at $j = h-1$; equivalently, their coefficients are zero.

For $0 \le r \le h-1$, let $\mathcal{P}_r$ denote the space of restrictions to the grid $\{0, 1, \dots, h-1\}$ of polynomials in j of degree at most r. This space has dimension $r+1$. We claim that $\mathcal{P}_r$ is invariant under A_h, and that the induced action on the quotient $\mathcal{P}_r / \mathcal{P}_{r-1}$ is multiplication by

$$h(h+1) - r(r+1).$$

It is enough to check the highest-degree term. Substituting $f(j) = j^r$ in (4) and expanding

$$\begin{aligned} (j-1)^r &= j^r - r j^{r-1} + \frac{r(r-1)}{2} j^{r-2} + \cdots, \\ (j+1)^r &= j^r + r j^{r-1} + \frac{r(r-1)}{2} j^{r-2} + \cdots, \end{aligned}$$

one sees that the coefficients of j^{r+2} and j^{r+1} cancel. The coefficient of j^r

is

$$-\frac{r(r-1)}{2}-hr-\frac{r(r-1)}{2}+r(h-2)+(h-1)+h^2+1$$
$$=h(h+1)-r(r+1).$$

Therefore $A_h\mathcal{P}_r\subseteq\mathcal{P}_r$ and, in the monomial flag

$$\mathcal{P}_0\subset\mathcal{P}_1\subset\cdots\subset\mathcal{P}_{h-1},$$

the diagonal entries of the matrix of A_h are

$$h(h+1)-r(r+1),\qquad r=0,1,\ldots,h-1.$$

Since A_h is a real symmetric $h\times h$ matrix, these diagonal entries are precisely its eigenvalues, counted with algebraic multiplicity. Finally, writing $k=h-r$ gives

$$h(h+1)-r(r+1)=k(2h+1-k),\qquad 1\le k\le h.$$

This proves (2). ■

Theorem 13 (Closed formula for linear acenes)**.** *Let A_h be the linear acene with $h\ge 1$ fused hexagons. Then*

$$\mathrm{RKf}_p(A_h)=8h^2(h+1)+2(2h+1)(h+1)$$
$$\times\left[\frac{1}{h+2}+(2h+3)\sum_{k=1}^{h}\frac{1}{h^2+3h+2-k(2h+1-k)}\right]. \tag{5}$$

In particular, the values in Table 4 are exact evaluations of (5)*.*

Proof. Use the standard two-row representation of A_h with upper vertices $u_0,\ldots,u_{2h}$, lower vertices $v_0,\ldots,v_{2h}$, horizontal edges u_iu_{i+1} and v_iv_{i+1}, and vertical fusion edges $u_{2j}v_{2j}$, $0\le j\le h$. A perfect matching contains exactly one vertical edge. Indeed, without a vertical edge the two horizontal paths have odd order. If two vertical edges $u_{2j}v_{2j}$ and $u_{2\ell}v_{2\ell}$, $j<\ell$, were selected, then the horizontal segment strictly between them would contain $2(\ell-j)-1$ vertices in each row, again leaving an odd path to be matched. Once the selected vertical edge is $u_{2j}v_{2j}$, all remaining horizon-

tal matching edges are forced. Hence there are $h+1$ perfect matchings, and the Pauling bond orders are

$$\begin{aligned} p_{u_{2i}u_{2i+1}} = p_{v_{2i}v_{2i+1}} &= \frac{h-i}{h+1}, \\ p_{u_{2i+1}u_{2i+2}} = p_{v_{2i+1}v_{2i+2}} &= \frac{i+1}{h+1}, \qquad 0 \le i \le h-1, \\ p_{u_{2j}v_{2j}} &= \frac{1}{h+1}, \qquad 0 \le j \le h. \end{aligned} \tag{6}$$

Let $N = 2h+1$. Reflection in the horizontal axis decomposes $L_p(A_h)$ into the orthogonal direct sum of a symmetric block and an antisymmetric block, corresponding respectively to the subspaces

$$\mathcal{S} = \{(x,x) : x \in \mathbb{R}^N\}, \qquad \mathcal{A} = \{(x,-x) : x \in \mathbb{R}^N\}.$$

Equivalently, the maps $x \mapsto 2^{-1/2}(x,x)$ and $x \mapsto 2^{-1/2}(x,-x)$ give orthonormal identifications of these two blocks with $\mathbb{R}^N$. Hence the trace of $L_p(A_h)^+$ is the sum of the inverse traces of the positive parts of the symmetric and antisymmetric blocks. On $\mathcal{S}$, the vertical edges contribute nothing because the endpoint values coincide, so the reduced matrix is the weighted path P_h on N vertices with conductances

$$c_{2i} = \frac{h-i}{h+1}, \qquad c_{2i+1} = \frac{i+1}{h+1}, \qquad 0 \le i \le h-1.$$

For a weighted path, the effective resistance between vertices $a < b$ is the sum of the reciprocal conductances along the unique a–b path. Summing this over all unordered pairs shows that each edge r contributes c_r^{-1} once for every pair separated by that edge, namely $(r+1)(N-r-1)$ pairs. Hence

$$N \operatorname{tr}(P_h^+) = \sum_{0 \le a < b \le N-1} R_{ab} = \sum_{r=0}^{N-2} (r+1)(N-r-1)c_r^{-1}.$$

Substituting the conductances above gives

$$N \operatorname{tr}(P_h^+) = 4h^2(h+1).$$

Since $n = 2N$, the symmetric contribution to $\mathrm{RKf}_p(A_h)$ is therefore $8h^2(h+1)$.

It remains to compute the antisymmetric block. On $\mathcal{A}$, a vector has the form $(x, -x)$, so a vertical edge of conductance $1/(h+1)$ joining u_{2j} and v_{2j} contributes

$$\frac{1}{h+1}(x_{2j} - (-x_{2j}))^2 = \frac{4}{h+1}x_{2j}^2$$

in the quadratic form, which corresponds to an additional diagonal term $2/(h+1)$ in the reduced antisymmetric matrix. Together with the horizontal conductances from (6), this shows that after multiplication by $h+1$, the antisymmetric block is the tridiagonal matrix C_h of order $2h+1$ whose diagonal entries are $h+2$ at even positions and $h+1$ at odd positions, and whose successive off-diagonal absolute values are

$$h, 1, h-1, 2, \ldots, 1, h.$$

Writing the even coordinates first and the odd coordinates second gives

$$C_h = \begin{pmatrix} (h+2)I_{h+1} & -X_h \\ -X_h^T & (h+1)I_h \end{pmatrix},$$

where X_h is the $(h+1) \times h$ bidiagonal matrix with $(X_h)_{j,j} = h - j$ and $(X_h)_{j+1,j} = j+1$ for $0 \le j \le h-1$. By Lemma 2, the nonzero eigenvalues of $X_h X_h^T$ are

$$\sigma_k = k(2h+1-k), \qquad 1 \le k \le h.$$

Besides the eigenvalue $h+2$ coming from $\ker X_h^T$, the remaining eigenvalues λ_k^-, λ_k^+ of C_h are determined by

$$(h+2-\lambda)(h+1-\lambda) = \sigma_k.$$

Therefore

$$\frac{1}{\lambda_k^-} + \frac{1}{\lambda_k^+} = \frac{2h+3}{(h+2)(h+1) - k(2h+1-k)}.$$

Since the antisymmetric block of the Pauling-weighted Laplacian is

$C_h/(h+1)$, its inverse trace is

$$(h+1)\left[\frac{1}{h+2}+(2h+3)\sum_{k=1}^{h}\frac{1}{h^2+3h+2-k(2h+1-k)}\right].$$

Multiplying by $n=2(2h+1)$ and adding the symmetric contribution gives (5). ∎

Corollary 14 (Leading growth of the linear-acene values)**.** *As $h\to\infty$,*

$$\mathrm{RKf}_p(A_h)=8h^3+O(h^{5/2}).$$

Proof. In the sum in (5), put $r=h-k$. Then

$$h^2+3h+2-k(2h+1-k)=r(r+1)+2(h+1),\qquad 0\le r\le h-1.$$

Consequently,

$$\sum_{k=1}^{h}\frac{1}{h^2+3h+2-k(2h+1-k)}=\sum_{r=0}^{h-1}\frac{1}{r(r+1)+2(h+1)}=O(h^{-1/2}),$$

for example by comparison with the integral of $(x^2+2h)^{-1}$. The second line of (5) is therefore $O(h^{5/2})$, while the first term is $8h^2(h+1)=8h^3+O(h^2)$. This proves the assertion. ∎

Figures 3 and 4 provide black-and-white numerical illustrations of the linear-acene family. Figure 3 compares the exact resonance-weighted values from Theorem 13 with the ordinary Kirchhoff index of the unweighted acene graph for $1\le h\le 12$. Figure 4 shows the ratio $\mathrm{RKf}_p(A_h)/\mathrm{Kf}(A_h)$ for $1\le h\le 20$. The plots are not used in any proof, but they visualize two robust features already suggested by the tables: the resonance-weighted invariant is larger than the ordinary Kirchhoff index, and the gap increases with chain length.

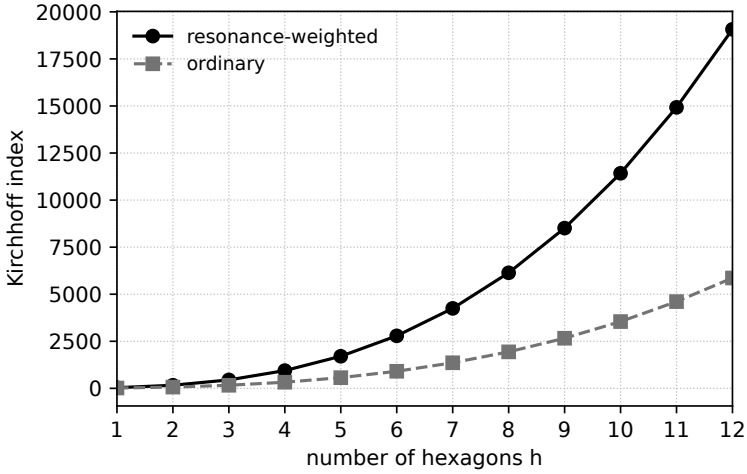

Figure 3. Black-and-white comparison of $\mathrm{RKf}_p(A_h)$ and the ordinary Kirchhoff index $\mathrm{Kf}(A_h)$ for the linear acenes A_h, $1 \le h \le 12$. The resonance-weighted values are exact evaluations of Theorem 13; the ordinary values are computed from the unweighted Laplacian of A_h.

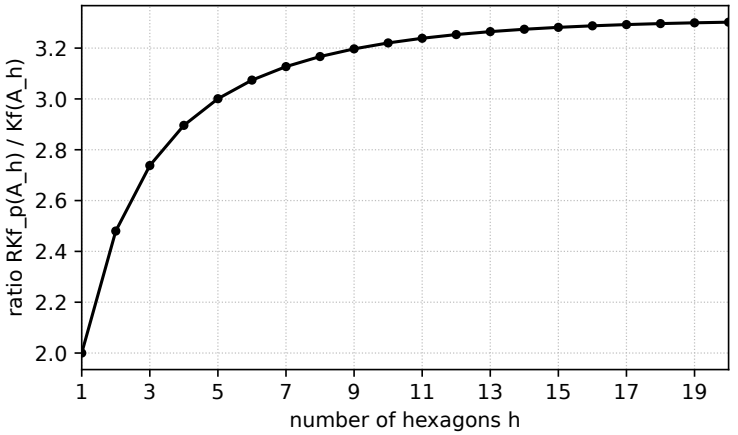

Figure 4. Black-and-white plot of the ratio $\mathrm{RKf}_p(A_h)/\,\mathrm{Kf}(A_h)$ for the linear acenes A_h, $1 \le h \le 20$. The finite-range plot illustrates the increase of the resonance-weighted value relative to the ordinary Kirchhoff index along this acene chain; no global monotonicity theorem is used in the paper.

Remark (Exact reproducibility of the benchmark values). The rational entries in Tables 1–4 are obtained from the displayed conductances by exact linear algebra. In particular, if L_p is formed over $\mathbb{Q}$, then

$$\mathrm{RKf}_p(G) = n \,\mathrm{tr}\left[\left(L_p + \frac{1}{n}J\right)^{-1} - \frac{1}{n}J\right] \tag{7}$$

with $J = \mathbf{1}\mathbf{1}^T$. This identity avoids numerical pseudoinversion and gives a direct check of every listed fraction. It is also a useful guard against the common scaling error in which uniform Pauling bond order is incorrectly treated as unit conductance.

7 Catacondensed benzenoids

Let $\mathcal{B}_h$ be the family of catacondensed benzenoid graphs with h hexagons. Every graph in $\mathcal{B}_h$ has

$$n = 4h + 2, \qquad m = 5h + 1.$$

Hence the mean Pauling bond order is

$$\overline{p} = \frac{1}{m}\sum_{e\in E} p_e = \frac{n}{2m} = \frac{4h+2}{10h+2},$$

which tends to $2/5$ as $h \to \infty$. This observation is useful because it corrects a tempting but erroneous $2/3$ limiting value.

The linear acene A_h is the unbranched catacondensed chain in which all hexagons are fused in a straight line. Angular chains, including helicene-type chains, distribute the Kekulé structures differently and typically create a more heterogeneous Pauling bond-order pattern. The comparison between anthracene and phenanthrene in Table 1 suggests that the resonance-weighted Kirchhoff index is sensitive to this heterogeneity.

The exact formula in Theorem 13 gives an infinite family of reference values. Nevertheless, it does not by itself compare the linear chain with all angular and branched catacondensed benzenoids. This point is important

because the ordinary unweighted Kirchhoff-index problem behaves differently: for hexagonal chains, the straight chain is known to maximize the ordinary Kirchhoff index, while the minimum is attained within the all-kink class [17, 18]. The available Pauling-weighted evidence is therefore limited, and the following statement is deliberately formulated as an open minimization problem rather than as a theorem or near-complete extremal principle.

Open Problem 1 (Linear-acene minimization problem)**.** *For every $h \geq 3$, the linear acene A_h minimizes the resonance-weighted Kirchhoff index over $\mathcal{B}_h$:*

$$\mathrm{RKf}_p(A_h) = \min\{\mathrm{RKf}_p(G) : G \in \mathcal{B}_h\}.$$

The open problem is motivated by two observations. First, linear acenes have a simple Kekulé structure count $h+1$, a highly ordered bond-order distribution, and the exact value given by Theorem 13. Second, angular fusion can create smaller positive bond orders on some bottleneck edges, and Theorem 7 shows that small conductances may enlarge the resistance sum substantially. These observations are not a substitute for an extremal proof, because the resistance contribution of a small conductance depends on its position in the whole weighted network.

The corresponding maximization problem over $\mathcal{B}_h$ may involve angular and branched chains with highly uneven Pauling bond-order distributions, but the present data do not determine a unique extremal family. A rigorous proof of Open Problem 1, or of any maximum theorem, would require a simultaneous analysis of the Pauling bond-order distribution and the effective resistances in the resulting weighted graph. This is not a straightforward extension of ordinary distance-based extremal results, because the edge weights themselves depend globally on the perfect-matching structure.

8 Concluding remarks and open problems

The resonance-weighted Kirchhoff index introduced in this paper is a natural specialization of weighted resistance distance to Kekuléan molecular

graphs. Its main feature is that the conductance of a bond is not imposed externally but is determined by the molecule's Kekulé structure ensemble. The invariant therefore combines two classical ideas: resistance distance and Pauling bond order.

The basic theory developed here shows that the invariant behaves in a controlled way. It is the Kirchhoff index of the average Laplacian of all Kekulé structures, it is strictly larger than the ordinary Kirchhoff index for nontrivial resonance-connected molecular graphs, and it satisfies support-dependent comparison bounds in terms of the extremal positive Pauling bond orders. The exact computations for small benzenoids demonstrate that the invariant is sensitive to structural changes that are only weakly reflected by the ordinary Kirchhoff index.

The limitations should also be clear. Pauling bond order is a combinatorial resonance descriptor rather than a quantum-chemical bond order, and the present paper proves structural and electrical properties of the resulting weighted graph invariant. Any quantitative chemical correlation with resonance energy, bond-length alternation, or experimentally measured quantities must be tested separately.

Several problems remain open.

(1) Resolve Open Problem 1; identify the maximum of RKf_p over $\mathcal{B}_h$.

(2) Extend the linear-acene formula in Theorem 13 to other catacondensed chains, especially helicene-type and branched families.

(3) Determine whether RKf_p has stronger correlation with resonance energy or bond-length alternation than Kf, the Wiener index, or the Szeged index on standard benzenoid data sets.

(4) Extend the construction from uniform Kekulé averaging to weighted resonance structures, such as Clar-weighted or energy-weighted Kekulé ensembles.

(5) Study the computational complexity of RKf_p and develop fast algorithms for large benzenoids, for example by Pfaffian or transfer-matrix methods.

These questions indicate that the proposed index is a useful and testable resistance-distance descriptor for resonance-sensitive chemical graph theory.

References

[1] R. B. Bapat, Resistance matrix of a weighted graph, *MATCH Commun. Math. Comput. Chem.* **50** (2004) 73–82.

[2] J. A. Bondy, U. S. R. Murty, *Graph Theory*, Springer, New York, 2008.

[3] D. Cvetković, M. Doob, H. Sachs, *Spectra of Graphs: Theory and Application*, Academic Press, New York, 1980.

[4] E. Estrada, L. A. Montero, Bond order weighted graphs in molecules as structure-property indices, *Mol. Eng.* **2** (1993) 363–373.

[5] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989.

[6] I. Gutman, B. Mohar, The quasi-Wiener and the Kirchhoff indices coincide, *J. Chem. Inf. Comput. Sci.* **36** (1996) 982–985.

[7] S. Huang, S. Li, On the resistance distance and Kirchhoff index of a linear hexagonal (cylinder) chain, *Physica A* **558** (2020) #124999.

[8] D. J. Klein, M. Randić, Resistance distance, *J. Math. Chem.* **12** (1993) 81–95.

[9] X. Li, A. F. Jalbout, Bond order weighted hyper-Wiener index, *J. Mol. Struct. Theochem* **634** (2003) 121–125.

[10] L. Lovász, M. D. Plummer, *Matching Theory*, North-Holland, Amsterdam, 1986.

[11] R. Merris, Laplacian matrices of graphs: a survey, *Lin. Algebra Appl.* **197–198** (1994) 143–176.

[12] B. Mohar, The Laplacian spectrum of graphs, in: Y. Alavi, G. Chartrand, O. R. Oellermann, A. J. Schwenk (Eds.), *Graph Theory, Combinatorics, and Applications*, Wiley, New York, 1991, pp. 871–898.

[13] L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, 1960.

[14] N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, 1992.

[15] D. Vukičević, J. Djurdjević, I. Gutman, Limitations of Pauling bond order concept, *Polycyc. Arom. Comp.* **32** (2012) 36–47.

[16] H. Wiener, Structural determination of paraffin boiling points, *J. Am. Chem. Soc.* **69** (1947) 17–20.

[17] Y. Yang, D. J. Klein, Comparison theorems on resistance distances and Kirchhoff indices of S,T-isomers, *Discr. Appl. Math.* **175** (2014) 87–93.

[18] Y. Yang, W. Sun, Minimal hexagonal chains with respect to the Kirchhoff index, *Discr. Math.* **345** (2022) #113099.

[19] Y. Yang, H. Zhang, Kirchhoff index of linear hexagonal chains, *Int. J. Quantum Chem.* **108** (2008) 503–512.