Chemical Graph Theory

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Section 13.1 Chemical Graph Theory

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INTRODUCTION

Chemical graph theory (CGT) is a branch of mathematical chemistry which deals with the nontrivial applications of graph theory to solve molecular problems. In general, a graph is used to represent a molecule by considering the atoms as the vertices of the graph and the molecular bonds as the edges. Then, the main goal of CGT is to use algebraic invariants to reduce the topological structure of a molecule to a single number which characterizes either the energy of the molecule as a whole or its orbitals, its molecular branching, structural fragments, and its electronic structures, among others. These graph theoretic invariants are expected to correlate with physical observables measures by experiments in a way that theoretical predictions can be used to gain chemical insights even for not yet existing molecules. In this brief review we shall present a selection of results in some of the most relevant areas of CGT.

13.1.1 Basic Definitions

DEFINITIONS

D1: A ***molecular graph*** $G = (V, E)$ is a simple graph having $n = |V|$ nodes and $m = |E|$ edges. The ***nodes*** $v_i \in V$ represent non-hydrogen atoms and the ***edges*** $(v_i, v_j) \in E$ represent covalent bonds between the corresponding atoms. In particular, hydrocarbons are formed only by carbon and hydrogen atoms and their molecular graphs represent the carbon skeleton of the molecule.

D2: An ***alternant conjugated hydrocarbon*** is a hydrocarbon with alternant multiple (double and/or triple) and single bonds, such as the molecular graph is bipartite and the edges of the graph represents $C = C$ and $= C - C =$ or $C \equiv C$ and $\equiv C - C \equiv$ bonds only.

13.1.2 Molecular Energy

FACTS

F1: In the Hückel Molecular Orbital (HMO) method for conjugated hydrocarbons the energy of the j^{th} molecular orbital of the so-called π-electrons is related to the graph spectra by

$$\lambda_j = \frac{\alpha - E_\pi(j)}{\beta},$$

where λ_j is an eigenvalue of the adjacency matrix of the hydrogen-depleted graph representing the conjugated hydrocarbon and α, β are empirical parameters [CoOlMa78, GrGuTr77, Ku06, Ya78].

F2: The total π (molecular) energy is given by

$$E_\pi = \alpha n_e + \beta \sum_{j=1}^{n} g_j \lambda_j + \beta E,$$

where n_e is the number of π-electrons in the molecule and g_j is the occupation number of the j^{th} molecular orbital.

F3: For neutral conjugated systems in their ground state [Gu05],

$$f(n) = \begin{cases} 2\sum_{j=1}^{n/2} \lambda_j & \text{if } n \text{ is even,} \\ 2\sum_{j=1}^{(n+1)/2} \lambda_j + \lambda_{(j+1)/2} & \text{if } n \text{ is odd.} \end{cases}$$

REMARKS

R1: In most of the conjugated molecules studied by HMO n is an even number. In such cases, E can be expressed as $E = \sum_{j=1}^{n} |\lambda_j|$.

R2: The concept of graph energy is defined for any graph as $E = \sum_{j=1}^{n} |\lambda_j|$ [Ni07]. In this case this term is not related to any "physical" energy but the index can be considered as a graph-theoretic invariant.

R3: $\beta < 0$, then in representing the energy of molecular orbitals $\varepsilon_j = \alpha + \beta\lambda_j$ it is assumed that the largest eigenvalue represents the minimum energy, then the second largest, and so forth [CoOlMa78, GrGuTr77, Ku06, Ya78].

R4: Because an alternant conjugated hydrocarbon has a bipartite molecular graph: $\lambda_j = -\lambda_{n-j+1}$ for all $j = 1, 2, \ldots, n$.

EXAMPLE

E1: The molecule of 1,3-butadiene is a conjugated hydrocarbon whose molecular graph is the path graph with four nodes P_4. The energy of the four molecular orbitals in 1,3-butadiene, expressed by the eigenvalues of the adjacency matrix are -1.618, -0.618, 0.618, 1.618. The total energy of the molecule is -4.472.

FACTS

F4: Let G be a graph with n vertices and m edges. Then [Mc71],

$$\sqrt{2m + n(n-1)(det\mathbf{A})^{n/2}} \leq E \leq \sqrt{mn}.$$

F5: Let G be a graph with m edges. Then, $2\sqrt{m} \leq E \leq 2m$.

F6: Let G be a graph with n vertices. Then, $E \geq 2\sqrt{n-1}$, where the equality holds if G is the star graph with n vertices.

F7: [KoMo01], $E \leq 2m/n + \sqrt{(n-1)(2m - 4m^2/n^2)}$ where the equality holds if and only if G is K_n, $\frac{n}{2}K_2$, or a strongly regular graph with two eigenvalues having absolute value

$$\sqrt{\frac{2m - (2m/n)^2}{n-1}}.$$

F8: Let G be a graph with n vertices. Then [KoMo01],

$$E \leq \frac{n}{2}(\sqrt{n} + 1),$$

where the equality holds if and only if G is a strongly regular graph with parameters

$$(n, (n + \sqrt{n})/2, (n + 2\sqrt{n})/4, (n + 2\sqrt{n})/4).$$

F9: Let G be a bipartite graph with n vertices and m edges. Then [KoMo03],

$$E \leq 4m/n + \sqrt{(n-2)(2m - 8m^2/n^2)}.$$

F10: For all sufficiently large n, there is a graph G of order n such that [Ni07]

$$E \geq \frac{n}{2}(\sqrt{n} - n^{1/10}).$$

13.1.3 Graph Nullity and Zero-Energy States

DEFINITION

D3: The ***nullity*** of a (molecular) graph, denoted by $\eta = \eta(G)$, is the algebraic multiplicity of the number zero in the spectrum of the adjacency matrix of the (molecular) graph.

REMARKS

R5: An alternant unsaturated conjugated hydrocarbon with $\eta = 0$ is predicted to have a stable, closed-shell, electron configuration. Otherwise, the respective molecule is predicted to have an unstable, open-shell, electron configuration.

R6: If n is even, then η is either zero or it is an even positive integer.

EXAMPLE

E2: The molecule of 1,3-cyclobutadiene is a conjugated hydrocarbon whose molecular graph is the cycle graph with four nodes c_4. The energy of the four molecular orbitals in 1,3-butadiene are $E_1 = \alpha - 2|\beta|$, $E_2 = \alpha + 0|\beta|$, $E_3 = \alpha + 0|\beta|$ and $E_4 = 4(\alpha + 2|\beta|)$. The nullity of this graph is $\eta = 2$ and the first orbital is occupied by a pair of electrons while the two zero-energy states have one electron each. The total π-energy is $E_\pi = 4(\alpha - |\beta|)$.

FACTS

F11: Let P_n, C_n and K_n be the path, cycle and complete graph with n vertices, respectively. Then [BoGu09],

i) $\eta(P_n) = 0$ if n is even and $\eta(P_n) = 1$ if n is odd.

ii) $\eta(C_n) = 2$ if $n \equiv 0$ $(mod\ 4)$ or *zero* otherwise.

iii) $\eta(K_1) = 1$ and $\eta(K_{n>1}) = 0$.

F12: [CvGu72] Let $M = M(G)$ be the size of the maximum matching of a graph, i.e., the maximum number of mutually non-adjacent edges of G. Let T be a tree with $n \geq 1$ vertices. Then, $\eta(T) = n - 2M$.

F13: [CvGuTr72] Let G be a bipartite graph with $n \geq$ vertices and no cycle of length $4s(s = 1, 2, \ldots)$, then $\eta(G) = n - 2M$.

REMARK

R7: The nullity of benzenoid graphs, which may contain cylces of length $4s$, is also given by $\eta(G) = n - 2M$ [Gu83, FaJoSa05].

FACTS

F14: [Lo50] Let G be a bipartite graph with incidence matrix $\mathbf{B}$, $\eta(G) = n - 2r(\mathbf{B})$, where $r(\mathbf{B})$ is the rank of $\mathbf{B}$.

F15: [ChLi07] Let G be a graph with n vertices and at least one cycle,

$$\eta(G) = \begin{cases} n - 2g(G) + 2 & g(G) \equiv 0 \ (mod\ 4), \\ n - 2g(G) & \text{otherwise} \end{cases}$$

where $g(G)$ is the *girth* (length of miminal cycle) of the graph.

F16: [ChLi07] If there is a path of length $d(p,q)$ between the vertices p and q of G

$$\eta(G) = \begin{cases} n - d(p,q) & \text{if } d(p,q) \text{ is even,} \\ n - d(p,q) - 1 & \text{otherwise.} \end{cases}$$

F17: [ChLi07] Let G be a simple connected graph of diameter D

$$\eta(G) = \begin{cases} n - D & \text{if } D \text{ is even,} \\ n - D - 1 & \text{otherwise.} \end{cases}$$

F18: [ChLi07] Let G be a simple connected graph on n vertices having K_p as a subgraph, where $2 \leq p \leq n$. Then,

$$\eta(G) \leq n - p.$$

13.1.4 Graph-Based Molecular Descriptors

DEFINITIONS

D4: A ***graph-based molecular descriptor***, commonly known as ***topological index*** (TI), is a graph-theoretic invariant characterizing numerically the topological structure of a molecule [DeBa00].

D5: The ***Wiener index*** of a (molecular) graph is a TI defined by

$$W = \sum_{i<j} d_{ij}$$

where d_{ij} is the ***shortest-path distance*** between the vertices i and j [Wi47].

D6: The ***Hosoya index*** of a (molecular) graph is a TI defined by

$$H = \sum_{i=0}^{n/2} P(G,i)$$

where $P(G,i)$ is the ***number of selections of*** i ***mutually nonadjacent edges*** in the graph. By definition $P(G,0) = 1$ and $P(G,1) = m$ [Ho71].

D7: The ***Zagreb indices*** of a (molecular) graph are TIs defined by [GuTr72]

$$M_1 = \sum_{j=1}^{n} (\delta_j)^2,$$

$$M_2 = \sum_{i,j \epsilon E} \delta_i \delta_j.$$

D8: The ***Randić*** index of a (molecular) graph is a TI defined by [Ra75]

$$\chi = \sum_{i,j \epsilon E} (\delta_i \delta_j)^{-1/2}.$$

D9: Let $k = 0, 1, 2, 3, \ldots$ is the number of adjacent vertices of degrees $\delta_i, \delta_j, \delta_l, \ldots$ in graph G. Then [KiHaMuRa75, KiHa76], the ***Kier and Hall molecular connectivity index*** is defined as

$$k_\chi = \sum_{i,j,l,\ldots} (\delta_i, \delta_j, \delta_l, \ldots)^{-1/2}$$

where the summation is taken over all subgraphs of size k, and the null term is the sum of all the vertex degrees (the total adjacency of G).

D10: Let $s_i = \sum\limits_{j=1}^{n} d_{ij}$, be the ***distance sum for the vertex*** i in a (molecular) graph. The ***Balaban index*** is a TI defined by

$$J = \frac{m}{C+1} \sum_{i,j \epsilon E}^{m} (s_i s_j)^{-1/2},$$

where $C = m - n + 1$ is the ***cyclomatic number*** of the graph [Ba82].

D11: The ***atom-bond connectivity index*** of a (molecular) graph is a TI defined by [EsToRoGu98, Es08a]

$$ABC = \sum_{i,j \epsilon E} \sqrt{\frac{\delta_i + \delta_j - 2}{\delta_i \delta_j}}.$$

D12: Let G be a connected graph with adjacency matrix $\mathbf{A}$ and let $\mathbf{D}$ be a diagonal matrix of vertex degrees of G. The ***Laplacian matrix*** of the graph is defined as $\mathbf{L} = \mathbf{D} - \mathbf{A}$.

D13: Let G be a connected graph with Laplacian matrix $\mathbf{L}$ and let p and q be two vertices of G. The ***resistance distance between*** p ***and*** q is defined by [KlRa93]

$$\Omega_{pq} = \mathbf{L}^\dagger_{pp} + \mathbf{L}^\dagger_{qq} - 2\mathbf{L}^\dagger_{pq}$$

where $\mathbf{L}^\dagger_{pq}$ is the p, q***-entry of the Moore-Penrose pseudo-inverse*** of the Laplacian matrix.

D14: The ***Kirchhoff index*** of a (molecular) graph is a TI defined by [KlRa93]

$$Kf = \sum_{i<j} \Omega_{ij}$$

REMARKS

R8: The Wiener number has been modified to describe the basic topology of infinite polymeric macromolecules and named *Wiener infinite*, W_∞ [BoMeKa92]:

$$W_\infty = \lim_{lim \to \infty} \frac{an^3 + bn^2 + cn + d}{m\left[\dfrac{n(n-1)}{2}\right]}$$

R9: The Randić index has been generalized to [BoErSa99]

$$\chi^t = \sum_{i,j \epsilon E} (\delta_i \delta_j)^t,$$

and a few mathematical results exist for the different values of t [LiSh08].

FACTS

F19: Let T_n be a tree with n vertices, then [EnJaSn76, BoTr77]

$$W(S_n) < W(T_n) < W(P_n),$$

where $W(S_n) = (n-1)^2$ and $W(P_n) = (\begin{matrix} n+1 \\ 3 \end{matrix})$

F20: Let T_n be a tree with n vertices and let $0 = \mu_1 < \mu_2 \leq \ldots \leq \mu_n$ be the eigenvalues of the Laplacian matrix of the tree. Then [Me90, Mo91, DoEnGu01],

$$W(T_n) = n \sum_{j=2}^{n} (\mu_j)^{-1}.$$

F21: Let H_k be a hexagonal chain with $k \geq 1$ linearly fused hexagons, then [ShLa97]

$$W(H_k) = \frac{1}{3}(16k^3 + 36k^2 + 26k + 3).$$

F22: Let T be a tree on n vertices. Let for an edge $e = (x, y)$ define $n_1(e) = |\{v|v \epsilon V(T), d(v, x|T) < d(v, y|T)$ and $n_2(e) = |\{v|v \epsilon V(T), d(v, y|T) < d(v, x|T)$. Then [Wi47, GuPo86, DoEnGu01],

$$W(T) = \sum_{e \epsilon E(T)} n_1(e) n_2(e)$$

REMARK

R10: This is the manner in which Wiener introduced his index in 1947.

FACTS

F23: Let T be a tree. Let the bipartite sets of its vertices are of cardinality $|V_a|$ and $|V_b|$. Then [BoGuPo87], $W(T)$ is odd if and only if both $|V_a|$ and $|V_b|$ are odd. If $|V_a|$ or/and $|V_b|$ is even, $W(G)$ is even.

F24: Let $m \geq 2$. Let $T_1, T_2, \ldots, T_m$ be trees with disjoint vertex sets and orders $n_1, n_2, \ldots, n_m$. Let for $i = 1, 2, \ldots, m, w_i \epsilon V(T_i)$. Let T be a tree on $n \geq 3$ vertices, obtained by joining a new vertex u to each of the vertices $w_1, w_2, \ldots, w_m$. Then [CaRoRo85, DoEnGu01],

$$W(T) = \sum_{i=1}^{m}[W(T_i) + (n - n_i)d(w_i|T_i) - n_i^2] + n(n-1)$$

F25: Let T be a tree on n vertices. Let v and u are vertices on a pendant edge. Then [DoGu94],

$$W(T) = \frac{1}{4}[n^2(n-1) - \sum_{(u,v)\epsilon E(T)} [d(v|T) - d(u|T)]^2].$$

F26: Let T be a tree on n vertices. Let $\deg(v)$ is the degree of vertex v. Then [KlMiPlTr92, DoGu94, Gu94],

$$W(T) = \frac{1}{4}[n(n-1) + \sum_{v\epsilon V(T)} \deg(v)d(v|T)]$$

F27: Let T be a tree on n vertices and u branching points. Then [DoGr77],

$$W(T) = \binom{n+1}{3} - \sum_{u} \sum_{1 \leq i < j < k \leq m} n_i n_j n_k.$$

F28: Let T be a tree on n vertices and let $L(T)$ is its line graph. Then [Bu81],

$$W(L(T)) = W(T) - \binom{n}{2}$$

F29: Let W_∞ be the Wiener infinite index, N_1 and C_1 the number of atoms and cycles in the monomeric unit, and d the distance between two neighboring monomeric units in the polymer graph. Then [BaBaBo01],

$$W_\infty = \frac{d}{3(N_1 + C_1)}.$$

F30: Let N, R_g^2, and W be the number of atoms of a polymer whose macromolecule contains no atomic rings, the mean-square radius of gyration of the polymer, and the Wiener number of the polymer graph. Let also b be the length of the covalent bond connecting two monomeric units, let c be the number of polymer chains in a unit volume, and let ξ be the friction coefficient. Then [BoMaDe02],

$$R_g^2 = \frac{b^2}{N^2}W; \eta_0 = \frac{cb^2\xi}{6N^2}W.$$

F31: Let g be the Zimm-Stockmayer branching ratio of a branched macromolecule containing no atomic rings. Let also W, W_{lin}, and R_g^2, $R_{g,lin}^2$ be the Wiener indices and the mean-square radius of gyration of the branched and linear polymer graph with the same molecular weight. Then [BoMaDe02],

$$g = \frac{R_g^2}{R_{g,lin}^2} = \frac{w}{w_{lin}}.$$

F32: Let subgraphs G_i cover upon a vertex u'. Let also $d(u\epsilon G)$ and $d(u_i\epsilon G_i)$ are the distance numbers of the common vertex u in graph G and its i^{th} component G_i. Then [PoBo86],

$$W(G) = \sum_i W(G_i) + nd(u \ \epsilon \ G) - \sum_i n_i d(u_i \ \epsilon \ G_i).$$

F33: Let I be the number of isomorphic components G', which cover to form graph H, and let each of the G's have n' vertices. Let also $W(G')$, $W(H)$, and $d(u|G')$ be the Wiener number of G' and H, and the distance number of vertex u in G'. Then [PoBo90],

$$W(H) = I.W(G') + (n'-1).I(I-1).d(u|G').$$

F34: Let graphs G_1 and G_2 have n_1 and n_2 vertices, and let the graphs be linked by a bridge $\{uv\}$. Then,

$$W(H) = W(G_1) + W(G_2) + n_1 n_2 + n_2 d(u|G_1) + n_1 d(v|G_2).$$

F35: Let an edge $\{uv\}$ be divided by an inserted vertex x. Let also, the total distance of vertex x in the graph H obtained by $d(xH)$, and the number of geodesics containing vertex s, which are enlarged due to the division of the edge be $b(s)$. Then,

$$W(H) = W(G) + d(x|H) + [\sum_{s\epsilon G} b(s)]/2.$$

F36: Let the edge considered in Fact 35 be a bridge. Let also the number of vertices in the two subgraphs G_1 and G_2 be n_1 and n_2, and let $u\epsilon G_1$ and $v\epsilon G_2$. Then,

$$W(H) = W(G) + n_1 n_2 + [d(u|G) + d(v|G) + n_1 + n_2]2.$$

F37: Let a subgraph of n_1 vertices be transferred from a terminal vertex u to another terminal vertex v. Let also the distance numbers of u and v be denoted by $d(u|G)$ and $d(v|G)$. Then [PoBo86],

$$\Delta W = n_1[d(u|G) - d(v|G)].$$

F38: Let a subgraph be transferred from a terminal vertex u to another terminal vertex v. Let also the length of the shortest path uv be L, the position of the branches located between u and v be i, and the number of vertices in these intermediate branches i, located symmetrically with respect to u and v be $n_{v,i}$ and $n_{u,i}$. Then [PoBo90],

$$\Delta W = \sum i[(L-2i)(n_{u,i} - n_{v,i})].$$

F39: Let T_n be a tree with n vertices and let F_n be the n^{th} Fibonacci number. Then,

$$n \leq Z(T_n) \leq F_n + 1$$

where the lower bound is obtained for S_n and the upper bound is obtained for P_n [Gu77].

F40: Let G be a graph with k components $G_1, G_2, \ldots, g_k$. Then [GuPo86],

$$Z(G) = \prod_{i=1}^{k} Z(G_i).$$

F41: Let G be a graph, let $pq\epsilon E$ be an edge and $p\epsilon V$ be a vertex of G [GuPo86]. Then,

i) $Z(G) = Z(G - pq) + Z(G - \{p, q\})$.

ii) $Z(G) = Z(G - p) + \sum_{p,q\epsilon E} Z(G - \{p, q\})$.

F42: Let G be a graph, let $pq\epsilon E$. Then, [WaYeYa10]

$$Z(G) \geq Z(G - pq).$$

F43: Let G be a graph with $|P_i|$ paths of length i, $|P_i| = m$, and $|C_3|$ triangles. Then [BrKeMeRu05],

i) $M_1 = 2m + 2|P_2|$,

ii) $M_2 = m + 2|P_2| + |P_3| + 3|C_3|$.

F44: Let G be a connected graph with n vertices and m edges, then [De98],

$$M_1 \leq m\left(\frac{2m}{n-1} + n - 2\right),$$

with equality if and only if the graph is S_n or K_n.

F45: [DaGu04] Let G be a graph with n vertices, then

$$0 \leq M_2 \leq \frac{1}{2}n(n-1)^3,$$

where the upper bound is obtained for the complete graph and the lower one for the empty graph.

F46: [DaGu04] Let G be a connected graph with n vertices, m edges and minimum degree δ_{min}, then

$$M_2 \leq 2m^2 - (n-1)m\delta_{min} + \frac{1}{2}(\delta_{min} - 1)m\left(\frac{2m}{n-1} + n - 2\right),$$

with equality if and only if the graph is S_n or K_n.

F47: Randić index is bounded as [CaGuHaPa03, LiSh08]

$$\sqrt{n-1} \leq \chi \leq \frac{n}{2}$$

where the lower bound is reached for the star S_n and the upper bound is attained for any regular network with n nodes indistinctly of its degree.

F48: Let T_n be a chemical tree ($\delta_{min} \leq 4$) with n vertices and $n_1 \geq 3$ pendant vertices. Then,

$$\chi(T_n) \leq \frac{n}{2} + n_1\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{6}} - \frac{7}{6}\right),$$

with equality if and only if the tree is $T(3, 2)$ [HaMe03].

F49: [Es10] Let $\mathbf{k} = \left[\delta_1^{-1/2}\ \delta_2^{-1/2} \ldots\ \delta_n^{-1/2}\right]^T$, then

$$\chi = \frac{1}{2}(n - \mathbf{k}^T\mathbf{L}\mathbf{k}).$$

F50: Let G be a connected graph with n vertices, m edges and let λ_1 the largest eigenvalue of the adjacency matrix of G. Then [FaMaSa93, CaHa04],

i) $\lambda_1 \geq \dfrac{m}{\chi}$,

ii) $\chi + \lambda_1 \geq 2\sqrt{n-1}$ $(n \geq 3)$,

iii) $\chi.\lambda_1 \geq n - 1 (n \geq 3)$.

F51: Let G be a connected graph with n vertices, then [DoGu10]

$$J(P_n) \leq J(G) \leq J(K_n),$$

where

$$J(P_n) = (n-1)\sum_{i=1}^{n-1}(s_i s_{i+1})^{-1/2},\ s_i = \frac{(n-i+1)(i-1)i}{2} + \frac{(i-1)i}{2}.$$

and

$$J(K_n) = \frac{n^2(n-1)}{2(n^2 - 3n + 4)}.$$

F52: [Da10] Let G be a connected graph with m edges and let δ_{max} be the maximum vertex degree. Then,

$$ABC \geq \frac{2^{7/4} m \sqrt{\delta_{max} - 1}}{\delta_{max}^{3/4} \left(\sqrt{\delta_{max}} + \sqrt{2} \right)}$$

when equality is attained for the path graph with n vertices.

F53: [ChGu11, DaGuFu11] Among graphs with n vertices the complete graph has the greatest ABC index and this maximal-ABC graph is unique.

F54: [ChGu11, DaGuFu11] The smallest ABC index for a connected graph with n vertices must be a tree and this minimal-ABC tree needs not be unique.

F55: [FuGrVu09] Among trees with n vertices, the star has the greatest ABC index and this maximal-ABC tree is unique.

REMARK

R11: The trees with vertices for which the ABC index is minimum are not known.

FACTS

F56: Let $\mathbf{L}(G-u)$ be the matrix resulting from removing the u^{th} row and column of the Laplacian and let $\mathbf{L}(G-u-v)$ the matrix resulting from removing both the u^{th} and v^{th} rows and columns of $\mathbf{L}$. The resistance distance can be calculated as [BaGuXi03]:

$$\Omega(u,v) = \frac{det\ \mathbf{L}(G-u-v)}{det\ \mathbf{L}(G-u)}.$$

F57: Let $U_k(u)$ be the u^{th} entry of the k^{th} orthonormal eigenvector associated to the Laplacian eigenvalue μ_k, which has been ordered as $0 = \mu_1 < \mu_2 \leq \ldots \leq \mu_n$. Then [XiGu03],

$$\Omega(u,v) = \sum_{k=2}^{n} \frac{1}{\mu_k} [U_k(u) - U_k(v)]^2.$$

F58: Let the resistance matrix $\mathbf{\Omega}$ be the matrix containing the resistance distance between every pair of vertices in a graph. Then [GoBoSa08],

$$\mathbf{\Omega} = |\mathbf{1}\rangle diag\{[\mathbf{L} + (1/n)\mathbf{J}]^{-1}\}^T + diag[\mathbf{L} + (1/n)\mathbf{J}]^{-1}\langle\mathbf{1}| - 2(\mathbf{L} + (1/n)\mathbf{J})^{-1}$$

where $\mathbf{J} = |\mathbf{1}\rangle\langle\mathbf{1}|$ is an all-ones matrix.

F59: Let G be a connected graph with n vertices, the Kirchhoff index is given by

$$Kf(G) = nTr \int_0^{\infty} \left(e^{-t\mathbf{L}} - \frac{1}{n} \mathbf{1}\mathbf{1}^T \right) dt,$$

where $\mathbf{1}$ is an all-ones column vector [GoBoSa08].

F60: Let G be a connected graph with $n \geq 3$ vertices, m edges, and let δ_{max} be the maximum vertex degree. Then [ZhTr08],

$$Kf(G) \geq \frac{n}{1+\delta_{max}} + \frac{n(n-2)^2}{2m-1-\delta_{max}}.$$

F61: Let G be a connected graph with $n \geq 2$ vertices, m edges, and let δ_{min} and δ_{max} be the minimum and maximum vertex degree, respectively. Let $0 = \mu_1 < \mu_2 \leq \ldots \leq \mu_n$ be the eigenvalues of the Laplacian matrix. Then [ZhTr09],

$$\frac{n}{\delta_{max}} \sum_{j=2}^{n} \frac{1}{\mu_j} \leq Kf(G) \leq \frac{n}{\delta_{min}} \sum_{j=2}^{n} \frac{1}{\mu_j},$$

with equalities at both sides if and only if is regular.

F62: Let G be a connected bipartite graph with $n \geq 2$ vertices, and let δ_{max} be the maximum vertex degree. Then [ZhTr09],

$$Kf(G) \geq \frac{n(2n-3)}{\delta_{max}},$$

with equality if and only if G is $K_{\frac{n}{2},\frac{n}{2}}$.

13.1.5 Walk-Based Molecular Parameters

DEFINITIONS

D15: A ***walk*** of length k is a sequence of (not necessarily distinct) nodes $v_0, v_1, \ldots, v_{k-1}, v_k$ such that for each $i = 1, 2, \ldots, k$ there is a link from v_{i-1} to v_i. A walk is ***closed*** if $v_0 = v_k$. The number of edges in the walk is named the ***length*** of the walk.

D16: The ***vector*** $w = [\mu_1, \mu_2, \ldots, \mu_k]$, where μ_j is the ***number of closed walks of length*** j or j^{th} ***spectral moment of the adjacency matrix*** in the graph and $k < \infty$, represents a molecular descriptor, such as a molecular property A can be expressed as

$$A = \sum_j b_j \mu_j + \alpha,$$

where b_j and α are ***empirical coefficients*** [GuTr72, JiTaHo84, BoKi92, Es08b].

REMARK

R12: Every μ_j can be expressed in terms of subgraphs, which allows to express a molecular property as a combination of fragmental molecular contributions.

DEFINITIONS

D17: The ***weighted sum*** of all closed walks starting at a given node represents an atomic descriptor, subgraph centrality, for the corresponding atom in a molecule [Es00, EsRo05],

$$EE_p = \sum_{k=0}^{\infty} \frac{(A^k)_{pp}}{k!} = (e^A)_{pp},$$

where e^A is a ***matrix function*** that can be defined using the following Taylor series:

$$e^A = I + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \ldots + \frac{A^k}{k!} + \ldots$$

D18: The ***sum of subgraph centralities*** of all atoms in a molecule is a molecular descriptor called the Estrada index of the graph [Es00, EsRo05, DeGuRa07],

$$EE(G) = \sum_{p=1}^{n} EE_p.$$

D19: The ***subgraph centrality*** and ***Estrada index*** have the following spectral representations [Es00, EsRo05, DeGuRa07]:

$$EE_p = \sum_{j=1}^{n} [\varphi_j(p)]^2 e^{\lambda j},$$

$$EE(G) = \sum_{j=1}^{n} e\lambda j.$$

REMARK

R13: The Estrada index of a molecular graph in which every edge is weighted by the parameter $\beta = (kT)^{-1}$, where T is the temperature and k is the Boltzmann constant, represents the electronic partition function of a molecule as defined by $Z_e = \sum_{j=1}^{n} e^{-\beta \epsilon_j}$ [EsHa07].

DEFINITIONS

D20: The ***probability*** that the system is found in a particular state can be obtained by considering a Maxwell-Boltzmann distribution [EsHa07]

$$p_j = \frac{e^{\beta \lambda_j}}{\sum_j e^{\beta \lambda_j}} = \frac{e^{\beta \lambda_j}}{EE(G, \beta)}.$$

D21: The ***enthalpy*** $H(G)$ and ***Helmholtz free energy*** $F(G)$ of the graph are, respectively [EsHa07]

$$H(G, \beta) = -\sum_{j=1}^{n} \lambda_j p_j,$$

$$F(G, \beta) = \beta^{-1} 1\text{n} EE.$$

FACTS

F63: [EsHi10] The Estrada index can be obtained as $EE = tr(e^{\beta \mathbf{A}})$, where tr is the trace and

$$exp(\mathbf{A}) = \sum_{k=0}^{\infty} \frac{\mathbf{A}^k}{k!}.$$

F64: [DeGuRa07] The Estrada index of a network G of size n is bounded as

$$n < EE(G) < e^{n-1} + \frac{n-1}{e},$$

where the lower bound is obtained for the graph having n nodes and no links and the upper bound is attained for the complete graph K_n.

F65: Let T_n be a tree with n vertices, then [De09, DeRaGu09]

$$EE(s_n) > EE(T_n) > EE(P_n),$$

where $EE(S_n) = n - 2 + 2\cosh(\sqrt{n-1})$, and $EE(P_n) = \sum_{r-1}^{n} e^{2\cos(2r\pi/(n+1))}$.

F66: [DeRaGu09] Let G be a graph with n vertices and m edges, then

$$\sqrt{n^2 + 4m} \leq EE(G_n) \leq n - 1 + e^{\sqrt{2m}}.$$

F67: [BeBo10] Let G be a graph with n vertices. Let δ_j be the degree of the j^{th} vertex and let $a, b \,\epsilon\, \mathbb{R}$ be such that the spectrum of $\mathbf{A}$ is contained in $[a, b]$. Then,

$$\sum_{j=1}^{n} \frac{b^2 e^{\frac{\delta_j}{b}} + \delta_j e^{-b}}{b^2 + \delta_j} \leq EE \leq \sum_{j=1}^{n} \frac{a^2 e^{\frac{\delta_j}{a}} + \delta_j e^{-a}}{a^2 + \delta_j}.$$

F68: [BeBo10] Let G be a graph with n vertices. Let δ_j be the degree of the j^{th} vertex and let $a = 1 - n$ and $b = n - 1$, then

$$\frac{(n-1)^2 e^{\frac{1}{n-1}} + e^{1-n}}{n-1} \leq EE \leq \frac{n-1}{e} . \frac{n-1+e^n}{n-2}.$$

F69: [EjFiLuZo07] Let G be a regular graph with n nodes of degree $d = q + 1$. Then,

$$EE(G, \beta) = n \left[\frac{q+1}{2\pi} \int_{-2\sqrt{q}}^{2\sqrt{q}} e^{\beta s} \frac{\sqrt{4q - s^2}}{(q+1)^2 - s^2} ds + \frac{1}{n} \sum_{\gamma} \sum_{k=1}^{\infty} \frac{i(\gamma)}{2^{kl(\gamma)/2}} I_{kl(\gamma)}(2\sqrt{q}\beta) \right],$$

where γ runs over all (oriented) primitive geodesics in the network, $l(\gamma)$ is the length of γ, and $I_m(z)$ is the Bessel function of the first kind

$$I_m(z) = \sum_{r=0}^{\infty} \frac{(z/2)^{n+2r}}{r!(n+r)!}.$$

F70: [EsHa07] The electronic parameters are bounded as:

i) $0 \leq S(G, \beta) \leq \beta \ln n$,

ii) $-\beta(n-1) \leq H(G, \beta) \leq 0$,

iii) $-\beta(n-1) \leq F(G, \beta) \leq -\beta 1 n n$,

the lower bounds are obtained for the complete graph as $n \to \infty$ and the upper bounds are reached for the null graph with n nodes.

13.1.6 Vibrational Analysis of Graphs

DEFINITIONS

D22: A ***ball-spring graph*** is a graph in which every node is a ball of mass m and every link is a spring with the spring constant $m\omega^2$ connecting two balls. The ball-spring graph is submerged into a thermal bath at the temperature T, such that the balls oscillate under thermal disturbances.

D23: The ***coordinates chosen to describe a configuration of the system are*** $x_i, i = 1, 2, \ldots, n$, each of which indicates the fluctuation of the ball i from its equilibrium point $x_i = 0$.

D24: The ***ball-spring graphs*** are described by any of the following Hamiltonians

$$H_A = \sum_i \left(\frac{p_i^2}{2m} + \frac{Km\omega^2}{2} x_i^2 \right) - \frac{m\omega^2}{2} \sum_{i,j} x_i A_{ij} x_j,$$

$$H_L = \sum_i \frac{p_i^2}{2m} + \frac{m\omega^2}{2} \sum_{i,j} x_i L_{ij} x_j,$$

where p_i is the ***momentum*** of the node i, K is a ***constant*** satisfying $K \geq max_i k_i$ and k_i is the ***degree*** of the node i [EsHaBe12].

D25: A ***classical vibrational scenario*** is one in which the momenta p_i and the coordinates x_i are independent variables. A ***quantum vibrational scenario*** is one in which the momentap_j and the coordinates x_i are not independent variables but they are operators that satisfy the commutation relation $[x_i, p_j] = i\hbar\delta_{ij}$, where $i = \sqrt{-1}, \hbar$ is the ***Dirac constant*** and δ_{ij} is the ***Dirac delta function*** [EsHaBe12].

FACT

F71: The mean displacement of node i in the classical vibrational scenario is given by any of the following expressions in dependence of the Hamiltonian selected [EsHaBe12]:

$$\Delta x_i = \sqrt{\langle x_i^2 \rangle} = \frac{1}{\beta m K \omega^2} \left[(I - A/K)^{-1} \right]_{ii},$$
$$\Delta x_i = \sqrt{\langle x_i^2 \rangle} = \frac{1}{\beta m \omega^2} \left[(L^{\dagger}) \right]_{ii},$$

where $L^{\dagger}$ is the Moore-Penrose generalized inverse of the Laplacian.

REMARK

R14: By obviating the physical constants the mean atomic displacements in the classical picture are given by the diagonal entries of the resolvent of the adjacency matrix or of the pseudoinverse of the Laplacian, respectively. The last expression was also investigated in [BaAtEr97, EsHa07].

FACT

F72: The mean displacement of node i in the quantum vibrational scenario is given by any of the following expressions in dependence of the Hamiltonian selected [EsHaBe12]:

$$\Delta x_i = \sqrt{\langle x_i^2 \rangle} = e^{-\beta \hbar \Omega} \left(\exp \left[\frac{\beta \hbar \omega^2}{2\Omega} A \right] \right)_{ii},$$
$$\Delta x_i = \sqrt{\langle x_i^2 \rangle} = \lim_{\Omega \to 0} \left(\exp \left[\frac{\beta \hbar \omega^2}{2\Omega} L \right] \right)_{pq},$$
$$= 1 + \lim_{\Omega \to 0} O_{2p} O_{2q} \exp \left[\frac{\beta \hbar \omega^2}{2\Omega} \mu_2 \right],$$

where μ_2 is the second eigenvalue of the Laplacian matrix and $\Omega = \sqrt{K/m\omega}$.

REMARK

R15: The displacement correlation between a pair of nodes $\langle x_i x_j \rangle$ is given by the i, j entry of the corresponding matrix [EsHaBe12].

FACTS

F73: The resistance distance between a pair of nodes in a graph can be expressed in terms of the node displacements due to small vibrations/oscillations as follows [EsHa07]

$$\Omega_{ij} = \left[(\Delta x_i)^2 + (\Delta x_j)^2 - \langle x_i x_j \rangle - \langle x_j x_i \rangle \right] = \left\langle (x_i - x_j)^2 \right\rangle.$$

F74: The sum of resistance distances for a given node in a graph, $R_i = \sum_{j=1}^{n} (L_{ii}^{\dagger} + L_{jj}^{\dagger} - 2L_{ij}^{\dagger})$ is related to the node displacements as [EsHa07]

$$R_i = n(\Delta x_i)^2 + \sum_{i=1}^{n} (\Delta x_i)^2 = n \left[(\Delta x_i)^2 + \overline{(\Delta x)^2} \right].$$

F75: The potential energy of the vibrations in a graph are given by [EsHa07]

$$\langle V(\overrightarrow{x}) \rangle = \frac{1}{2n} \sum_{i=1}^{n} k_i R_i - \frac{1}{2n} \sum_{i,j \epsilon E} (R_i + R_j - n\Omega_{ij}).$$

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GLOSSARY FOR SECTION 13.1

ABC index - atom-bond connectivity index: the sum of the square root of edge weights for the graph, where the edge weights are defined as the edge degree divided by the product of vertex degrees of the pair of vertices forming the edge.

alternant conjugate molecule: a molecule in which multiple bonds (double or triple) alternates with single ones.

Balaban index: an analog of the Randić index in which the vertex degrees are replaced by the total distances of the graph vertices, with a normalizing coefficient including the number of graph edges and cycles of a molecule.

benzenoid molecule: a molecule formed by fused hexagonal rings.

bipartite graph: a graph with two sets of vertices, the nodes of each set being connected only to nodes of the other set.

complete graph: a graph in which every pair of vertices are connected to each other.

cycle: a path in which the initial and end vertices coincide.

cycle graph: a graph in which every node has degree two.

displacement correlation: refers to the correlation function of the displacements of two atoms (vertices) in a molecule.

edge degree: number of edges adjacent to a given edge.

Estrada index: the sum of the exponential of the eigenvalues of the adjacency matrix., i.e., the trace of the exponential of the adjacency matrix.

graph diameter: the length of the largest shortest-path distance in a graph.

graph energy: the sum of the absolute values of graph eigenvalues.

graph invariant: a characterization of a graph which does not depends on the labelling of vertices or edges.

graph nullity: the multiplicity of the zero eigenvalue of the adjacency matrix, i.e., the number of times eigenvalue zero occurs in the spectrum of the adjacency matrix.

molecular Hamiltonian: is the operator representing the energy of the electrons and atomic nuclei in a molecule.

Hosoya index: the total number of selections of k mutually nonadjacent edges with k (max) equal to the half of the number of vertices in the graph.

hydrocarbon: a molecule formed only by carbon and hydrogen.

incidence matrix: of a graph: a matrix whose rows correspond to vertices and its columns to edges of the graph and the i, j entry is one or zero if the i^{th} vertex is incident with the j^{th} edge or not, respectively.

Kirchhoff index: the sum of the resistances of the graph.

Laplacian matrix: a square symmetric matrix with diagonal entries equal to the degree of the corresponding vertex and out-diagonal equal to -1 or zero depending if the corresponding vertices are connected or not, respectively.

matching of a graph: the number of mutually non-adjacent edges in the graph.

mean displacement - of an atom (vertex): refers to the oscillations of an atoms from its equilibrium position due to thermal fluctuations.

molecular descriptor: a quantitative characteristic of a molecule based on its structure or composition.

molecular graph: simple graph with non-hydrogen atoms as nodes and covalent bonds between them representing links .

path: a sequence of different consecutive vertices and edges in a graph.

path graph: a graph formed by vertices a degree two except two nodes of degree one.

Randić index: the sum of inverse-square root of the product of degrees of all pairs of vertices in the graph.

resistance distance: a distance between any pair of vertices of the graph, determined by the Kirchhoff rules for electrical sets.

shortest path: a path having the least number of edges among all paths connecting two vertices.

simple graph: a graph without multiple edges, self-loops and weights.

star graph: a tree consisting of a node with degree n-1 and n-1 nodes with degree one.

strongly regular graph: a regular graph in which every two adjacent vertices, and every two non-adjacent vertices have an integer number of common neighbors.

subgraph centrality - of a vertex: the corresponding diagonal entry of the exponential of the adjacency matrix.

topological index: a graph invariant characterizing numerically the topological structure of a molecule.

tree: a graph that does not have any cycle.

walk: a sequence of (not necessarily) different consecutive vertices and edges in a graph.
Wiener index: the sum of the shortest-path distances between all pairs of vertices in the graph.

Zagreb indices: a pair of topological indices based on sums of squared vertex degrees or the product of vertex degrees of adjacent vertices.