



This is a repository copy of *In search of Coulson's lost theorem*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/157478/>

Version: Published Version

Article:

Fowler, P.W. orcid.org/0000-0003-2106-1104 and Pickup, B.T. orcid.org/0000-0002-2728-5486 (2019) In search of Coulson's lost theorem. *The Journal of Chemical Physics*, 151 (15). 151101. ISSN 0021-9606

<https://doi.org/10.1063/1.5128624>

This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. The following article appeared in *J. Chem. Phys.* 151, 151101 (2019) and may be found at <https://doi.org/10.1063/1.5128624>.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

In search of Coulson's lost theorem

Cite as: J. Chem. Phys. **151**, 151101 (2019); <https://doi.org/10.1063/1.5128624>

Submitted: 20 September 2019 . Accepted: 25 September 2019 . Published Online: 15 October 2019

Patrick W. Fowler , and Barry T. Pickup 



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Adventures in DFT by a wavefunction theorist](#)

The Journal of Chemical Physics **151**, 160901 (2019); <https://doi.org/10.1063/1.5116338>

[Fantasy versus reality in fragment-based quantum chemistry](#)

The Journal of Chemical Physics **151**, 170901 (2019); <https://doi.org/10.1063/1.5126216>

[Perspective: Computational chemistry software and its advancement as illustrated through three grand challenge cases for molecular science](#)

The Journal of Chemical Physics **149**, 180901 (2018); <https://doi.org/10.1063/1.5052551>

Lock-in Amplifiers

Find out more today



 Zurich
Instruments

In search of Coulson's lost theorem

Cite as: J. Chem. Phys. 151, 151101 (2019); doi: 10.1063/1.5128624

Submitted: 20 September 2019 • Accepted: 25 September 2019 •

Published Online: 15 October 2019



View Online



Export Citation



CrossMark

Patrick W. Fowler^{a)}  and Barry T. Pickup^{b)} 

AFFILIATIONS

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom

^{a)} Author to whom correspondence should be addressed: P.W.Fowler@sheffield.ac.uk

^{b)} Electronic mail: B.T.Pickup@sheffield.ac.uk

ABSTRACT

In Hückel theory, the bond number is the sum of the orders of the π bonds incident on a given carbon center. From the work of Coulson and his school, it has been believed for over 70 years that the bond number has a maximum of $\sqrt{3}$ and that this bound is realized by exactly one conjugated framework, that of the trimethylenemethane radical. Search of published literature and archived correspondence failed to find any formal proof of these two statements. Here, we provide a new formula for bond number that leads to an easily checked proof of both. The bond number of graphene is 1.574 597... (90.9% of the mathematical limit), and this value appears to act as a separator for the classes of metallic and semiconducting single-walled nanotubes, as defined within Hückel theory.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5128624>

I. INTRODUCTION

Electronic properties of π conjugated hydrocarbons and carbon nanostructures, from polycyclic aromatics¹ and fullerenes² to nanotubes,³ nanocones,⁴ and graphenes,⁵ can now be calculated at high levels of sophistication,⁶ but qualitative models such as Hückel theory are still giving valuable insights for these systems. Hückel Molecular Orbital (HMO) theory is a tight-binding model, with eigenvectors and eigenvalues of the adjacency matrix of the molecular graph corresponding to the π molecular orbitals and their energies, respectively. Coulson and his school exploited the HMO model extensively in the middle of the last century to develop concepts of bonding theory⁷ that are still used; many of their definitions were based on exact mathematical results, such as the famous pairing theorem.⁸ Here, we investigate a theorem about the maximum bond number, which first surfaced in a note-in-proof to a 1948 Coulson paper⁹ and enjoyed a shadowy existence over the next 70 years in papers, reviews, and textbooks. That theorem is finally proved here and shown to correspond to a universal limit for carbon nanostructures, finite and infinite. For single-walled carbon nanotubes (SWCNT), for example, bond number turns out to be a natural separator of metallic and semiconducting behavior at the Hückel level.

Bond number, N_r , is the sum of mobile π bond orders over the bonds at a given center, and its deviation from the maximum possible value is the free valence, an indicator of availability for further bond formation by radical addition.¹⁰ In its strongest form,

the claim in Coulson's footnote⁹ is that, within HMO theory, the maximum π bond number achievable in an unsaturated framework by carbon atom r with d_r carbon neighbors is $\sqrt{d_r}$, and that maxima of $\sqrt{1}$, $\sqrt{2}$, and $\sqrt{3}$ for primary, secondary, and tertiary carbon atoms are realized uniquely in three π systems [ethene, allyl, and 2-methylenyl-1,3-propenyl (trimethylenemethane)]. Coulson had thought that the global maximum was 1.680. His footnote attributes recent proof of the higher $\sqrt{3}$ limit to his student Moffitt, whose thesis¹¹ had not mentioned this number, although it appears in two sentences added in the journal version,¹² in a plausibility argument, based on presumed dilution of central bonding by second neighbors. The $\sqrt{3}$ maximum was featured in chemistry texts for decades, where it was variously described as arbitrary, assumed, convenient, conventional, a definition, obvious, proved, or easily provable. A second footnote, this time in a textbook,¹³ implies that in 1963, Coulson mentioned that the $\sqrt{3}$ limit could be proved (albeit with difficulty) using contour integration. This is clearly not the Moffitt "proof" referred to in 1948. When was it done? Was it ever published? 20 years later, a paper by Gutman¹⁴ gives a partial mathematical proof, valid for acyclic systems only; a footnote concludes that any earlier proof is probably lost. The main actors in the story are no longer available for comment,¹⁵⁻¹⁷ and search in the Bodleian archive,¹⁸ which includes Coulson's own copies of correspondence with relevant individuals, revealed no discussion of a proof, even during preparation of a landmark paper on free valence.¹⁰ We can now provide that proof.

II. METHOD

In the Hückel model, atomic p_π basis functions, χ_r , on carbon centers $r = 1, \dots, n$ are used to construct molecular orbitals ϕ_k as linear combinations,

$$\phi_k = \sum_{r=1}^n U_{rk} \chi_r, \quad (1)$$

where unitary matrix U diagonalizes $A(G)$, the adjacency matrix of the molecular graph, G ,

$$\begin{aligned} \mathbf{A}U &= U\boldsymbol{\lambda} \text{ with } U U^\dagger = U^\dagger U = \mathbf{1} \text{ and} \\ \boldsymbol{\lambda} &= U^\dagger \mathbf{A}U \text{ with } (\boldsymbol{\lambda})_{jk} = \lambda_k \delta_{jk}. \end{aligned} \quad (2)$$

Eigenvalues λ_k ($k = 1, \dots, n$) are in nonincreasing order. \mathbf{A} has entries $A_{rs} = 1$ for pairs $r \sim s$ of vertices (carbon atoms) connected by an edge (π bond), and $A_{rs} = 0$ otherwise. Orbital energies are

$$\epsilon_k = \alpha + \lambda_k \beta, \quad (3)$$

where α and β are Coulomb and resonance integrals, both negative energy quantities, taken as the zero and unit of the energy scale, and orbitals of equal energy form a shell. Positive, zero, and negative eigenvalues are associated with bonding, nonbonding, and antibonding orbitals, respectively. Orbitals are filled with electrons according to aufbau, Pauli, and Hund's rules, to give occupation numbers $n_k = 2, 1, 0$. In the case of partial occupation, a configurational average assigns equal fractional occupancy to all members of the shell. Energy, atomic populations, and bond orders of the π system are calculated from

$$\begin{aligned} E_\pi &= \sum_{k=1}^n n_k \lambda_k, \\ q_r &= \sum_{k=1}^n n_k |U_{rk}|^2, \\ p_{rs} &= \sum_{k=1}^n n_k U_{rk} U_{sk}^*. \end{aligned} \quad (4)$$

From the secular equations, a local adjacency condition holds at each vertex,

$$\lambda_k U_{rk} = \sum_{s \sim r} U_{sk}. \quad (5)$$

Another relation arising from Eq. (2) is

$$A_{rr} = (\mathbf{U} \boldsymbol{\lambda} U^\dagger)_{rr} = \sum_{k=1}^n |U_{rk}|^2 \lambda_k = 0. \quad (6)$$

The π bond number for vertex r is therefore

$$N_r = \sum_{s \sim r} p_{rs} = \sum_{k=1}^n n_k |U_{rk}|^2 \lambda_k, \quad (7)$$

and its maximum value, \tilde{N}_r , achieved in the "natural" electronic configuration with $n_k = 2$ for $\lambda_k > 0$, $n_k = 1$ for $\lambda_k = 0$, and $n_k = 0$ for $\lambda_k < 0$ is, using Eq. (7),

$$\tilde{N}_r = \sum_{k=1}^n |U_{rk}|^2 |\lambda_k| \geq N_r. \quad (8)$$

For bipartite graphs (alternant molecules), this configuration is the ground-state configuration of the neutral species, and for all graphs, it maximizes all bond numbers and π energy. This maximum is the so-called graph energy,¹⁹

$$E_G = \sum_{k=1}^n |\lambda_k| \geq E_\pi. \quad (9)$$

Energy can be calculated from the electron distribution as⁷

$$\begin{aligned} E_\pi &= \sum_{s \sim r} p_{rs} A_{sr} + q_r A_{rr} = \sum_r N_r \text{ and} \\ E_G &= \sum_r \tilde{N}_r \end{aligned} \quad (10)$$

so that the bond number is the contribution of the conjugated atom r to total π energy. Our aim here was to prove a bound on \tilde{N}_r valid for any G (simple, connected, and unweighted) and any vertex of finite degree d_r . We based the proof on a contour-integral formula for bond number first given by Coulson,⁹ but details of the derivation are immaterial, as once obtained, the formula is self-checking: it provides a bound that is sharp and can be shown to be uniquely realized for degrees 1, 2, and 3 by the "chemical stars," C_2H_4 , C_3H_5 , and $C(CH_2)_3$.

III. THE RESULT

The new formula for the maximum bond number for vertex r of degree $d_r = a_r^2$ is

$$\tilde{N}_r = a_r - \frac{1}{2a_r} \sum_{k=1}^n (a_r - |\lambda_k|)^2 |U_{rk}|^2, \quad (11)$$

where $\{\lambda_k\}$ are eigenvalues and $\{U_{rk}\}$ are eigenvector entries. This is the cornerstone for the missing theorem, as it immediately gives the required upper bound for \tilde{N}_r (and N_r), since the terms under the summation sign are squares, hence strictly non-negative.

Correctness is easily checked by expanding the summation. By row normalization,

$$\sum_{k=1}^n a_r^2 |U_{rk}|^2 = a_r^2. \quad (12)$$

From Eq. (8),

$$\sum_{k=1}^n 2a_r |\lambda_k| |U_{rk}|^2 = 2a_r \tilde{N}_r. \quad (13)$$

Finally, $\boldsymbol{\lambda} = U^\dagger \mathbf{A}U$ gives a reduction of the third term,

$$\begin{aligned} \sum_{k=1}^n |\lambda_k|^2 |U_{rk}|^2 &= \sum_{k=1}^n \lambda_k^2 |U_{rk}|^2 \\ &= \left[\mathbf{U} (\mathbf{U}^\dagger \mathbf{A}U) (\mathbf{U}^\dagger \mathbf{A}U) \mathbf{U}^\dagger \right]_{rr} \\ &= (\mathbf{A}^2)_{rr} = d_r, \end{aligned} \quad (14)$$

as entries in the squared adjacency matrix count walks of length 2.

Hence, Eq. (11) reduces to the tautology,

$$\tilde{N}_r = a_r - \frac{a_r}{2} + \tilde{N}_r - \frac{a_r}{2},$$

and the bound is proved.

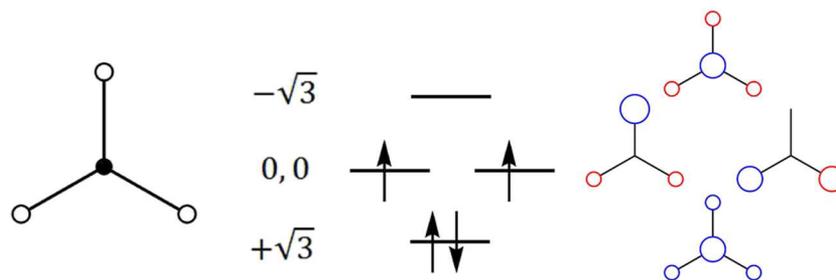


FIG. 1. Trimethylenemethane; the left panel is the molecular graph (i.e., the star on four vertices); the middle panel gives the Hückel energy-level diagram for the diradical species, showing eigenvalues and orbital occupancies; the right panel shows the corresponding eigenvectors, with small, medium, and large circles representing entries $1/\sqrt{6}$, $1/\sqrt{2}$, and $2/\sqrt{6}$, respectively, oppositely signed for colors red and blue. The vectors, combined with the occupancies, yield π -bond orders $1/\sqrt{3}$ for all three edges of the molecular graph.

The next stage is to check that the bound is sharp. To do this, we need some definitions. A *star* graph S_r has central vertex r with $d_r = n - 1$ neighbors of degree 1 and eigenvalues $(\pm a_r, 0^{d_r-1})$ (see Fig. 1). The chemical stars are ethene, allyl, and trimethylenemethane, with graphs K_2 , P_3 , and S_4 , respectively. The central vertex of any star is *core-forbidden*. A core-forbidden vertex (CFV) has entry zero in all eigenvectors in the nullspace (the shell of eigenvectors with zero eigenvalue).²⁰ In chemical terms, equal occupation of all orbitals in the nonbonding shell would give zero contribution to charge- or spin-density on a CFV. The generalization to other shells is the λ_k -forbidden vertex (λ_k -CFV): a vertex that has $U_{rk'} = 0$ for every vector with eigenvalue $\lambda_{k'} = \lambda_k$. In this language, the k th term in the sum in Eq. (11) vanishes if either the eigenvalue satisfies $|\lambda_k| = a_r$ or the vertex r is a λ_k -CFV. Hence, the star has $\tilde{N}_r = a_r$, meeting the bound.

The final stage is to check that stars are the *only* graphs that realize the bound. The argument here is slightly more involved. First, note that every connected graph G has nondegenerate maximum (Perron) eigenvalue λ_1 , with a strictly positive eigenvector ($U_{r1} > 0$ for all r).²¹ Thus, any graph for which $\lambda_1 \neq a_r$ has at least one nonzero term under the summation in Eq. (11) and cannot meet the bound. Let H be a graph that meets the bound for vertex r with degree d_r . It must have $\lambda_1 = a_r$.

Suppose first that H is nonbipartite. Then, $-a_r$ is not an eigenvalue,²¹ and r must be a λ_k -CFV for all $k \neq 1$. Row normalization then gives $U_{r1} = 1$, leaving no room in the Perron eigenvector for other vertices, so H is an isolated vertex, a contradiction.

Suppose instead that H is bipartite. By the pairing theorem,⁸ $\lambda_n = -a_r$, $|U_{r1}|^2 = |U_{rn}|^2$, and, since r is a λ_k -CFV for the intermediate eigenvalues, $1 < k < n$, we have $|U_{rk}|^2 = 0$ and hence $U_{r1} = U_{rn} = 1/\sqrt{2}$. The local sum rule Eq. (5) at vertex r gives

$$\lambda_k U_{r1} = \sum_{s \sim r} U_{s1} = \frac{a_r}{\sqrt{2}} \quad (15)$$

with all $U_{s1} > 0$; normalization of the Perron eigenvector gives

$$\sum_{s \neq r} |U_{s1}|^2 = \frac{1}{2} \quad \text{and} \quad \sum_{s \sim r} |U_{s1}|^2 \leq \frac{1}{2}. \quad (16)$$

As Eqs. (15) and (16) define a hyperplane and a ball in the d_r -dimensional space, respectively, a geometrical argument gives a

unique solution as the tangent point where $U_{s1} = (\sqrt{2}a_r)^{-1}$, implying degree 1, for all vertices $s \sim r$. Hence, H is the bipartite graph consisting of r and its neighborhood, i.e., the star on $d_r + 1$ vertices.

IV. CONCLUSIONS

Our proof retains the spirit of Moffitt's intuition¹² about dilution of bonding in the lowest occupied orbital (Fig. 2) but shows that any molecular graph meeting the bound must obey strict conditions on all eigenvector entries and eigenvalues. Significantly, the bound is valid for all conjugated carbon nanostructures and can be applied to 1D, 2D, and 3D infinite systems such as nanotubes, graphene, and more exotic allotropes²² by taking the band-theory limit. Graphene falls considerably short of the $\sqrt{3}$ limit with a value of \tilde{N}_r of 1.574 597. Progression from the highly curved smallest fullerene C_{20}^{2+} (1.470 820) through C_{60} (1.552 693) to graphene changes \tilde{N}_r from 85%, to 90%–91% of the limit, in line with the expected trend of reactivity with the curvature.²³ Graphene also provides a separator for conducting behavior in single-walled nanotubes (Fig. 3). In HMO theory, nanotubes obey a leapfrog-type rule: those with Hamada²⁵ indices $n_1 - n_2 = 0 \pmod{3}$ are predicted metallic, and others semiconducting. This turns out to be an oversimplification,²⁴ but it is notable that the semiconducting and metallic tubes on this criterion lie, respectively, above and below the graphene limiting value.

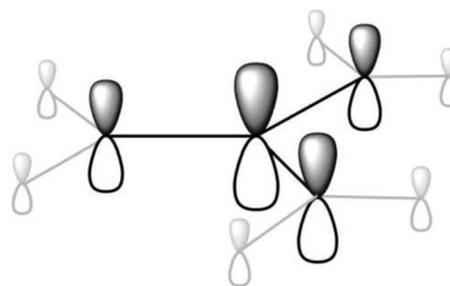


FIG. 2. Moffitt's intuitive picture of bonding at an unsaturated carbon site. Addition of second neighbors leads to the depletion of bonding density between the central atom and its immediate neighbors and lowering of the bond number.

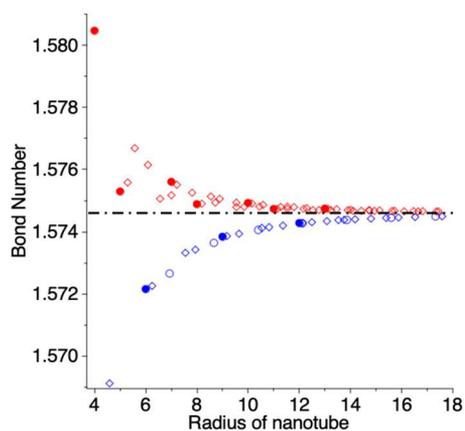


FIG. 3. Bond numbers of nanotubes calculated using the methods of Ref. 24. The combinatorial radius of a nanotube with Hamada indices²⁵ (n_1, n_2) is $(n_1^2 + n_1 n_2 + n_2^2)^{1/2}$, convertible to a physical radius by multiplication with R_{CC}/π , where R_{CC} is the bond length. The broken line is the graphene limit. Symbols above/below the line represent Hückel semiconductors and metals, respectively. Filled circles denote zigzag tubes $(n_1, 0)$, open circles denote armchair tubes (n_1, n_1) , and diamonds denote chiral tubes with unequal nonzero indices (n_1, n_2) . All tubes with $4 \leq n_1 \leq 13$ and combinatorial radius ≤ 18 are included in the plot.

Finally, we note that, with a few small changes, Eq. (11) can be extended to graphs with edge and vertex weights, exploiting the definition [Eq. (10)] of the bond number in terms of atomic contribution to π energy. This allows treatment of finite and infinite systems with bond alternation, such as polyacetylene, or electronegativity alternation, such as single-layer hexagonal boron nitride.

REFERENCES

- L. Zhang, Y. Cao, N. Colella, Y. Liang, J.-L. Brédas, K. Houk, and A. Briseno, "Unconventional chemically stable, and soluble two-dimensional angular polycyclic aromatic hydrocarbons: From molecular design to device applications," *Acc. Chem. Res.* **48**, 500–509 (2014).
- H. Kroto, J. Heath, S. O'Brien, R. Curl, and R. Smalley, " C_{60} -buckminsterfullerene," *Nature* **318**, 162–163 (1985).
- S. Iijima, "Helical microtubules of graphitic carbon," *Nature* **354**, 56–58 (1991).
- A. Krishnan, E. Dujardin, M. Treacy, J. Hugdahl, S. J. Lynam, and T. Ebbesen, "Graphitic cones and the nucleation of curved carbon surfaces," *Nature* **388**, 451–454 (1997).
- K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, and A. Firsov, "Electric field effect in atomically thin carbon films," *Science* **306**, 666–669 (2004).
- T. Dinadayalane and J. Leszczynski, "Fundamental structural, electronic, and chemical properties of carbon nanostructures: Graphene, fullerenes, carbon nanotubes, and their derivatives," in *Handbook of Computational Chemistry*, edited by J. Leszczynski, A. Kaczmarek-Kedziera, T. Puzyn, M. Papadopoulos, H. Reis, and M. Shukla (Springer International Publishing, 2017).
- C. Coulson and H. Longuet-Higgins, "The electronic structure of conjugated systems I. General Theory," *Proc. R. Soc. London, Ser. A* **191**, 39–60 (1947); "The electronic structure of conjugated systems II. Unsaturated Hydrocarbons and their Hetero-Derivatives," **192**, 16–32 (1947); C. Coulson, "The electronic theory of conjugated systems III. Bond orders in unsaturated molecules," *J. Chim. Phys. Phys.-Chim. Biol.* **193**, 447–456 (1948); C. Coulson and H. Longuet-Higgins, "The electronic structure of conjugated systems IV. Force constants in unsaturated hydrocarbons," *Proc. R. Soc. London, Ser. A* **193**, 453–464 (1948); "The electronic structure of conjugated systems V. The interaction of two conjugated systems," **195**, 188–197 (1949).
- C. Coulson and G. Rushbrooke, "Note on the method of molecular orbitals," *Math. Proc. Cambridge Philos. Soc.* **36**, 193–200 (1940); R. Mallion and D. Rouvray, "The golden jubilee of the Coulson-Rushbrooke pairing theorem," *J. Math. Chem.* **5**, 1–21 (1990).
- C. Coulson, "Free valence in organic reactions," *J. Chim. Phys. Phys.-Chim. Biol.* **45**, 247–248 (1948).
- F. Burkitt, C. Coulson, and H. Longuet-Higgins, "Free valence in unsaturated hydrocarbons," *Trans. Faraday Soc.* **47**, 553–564 (1951).
- W. Moffitt, *On the Electronic Structure of Molecules*, DPhil thesis, Oxford University, 1948.
- W. Moffitt, "The residual affinity of conjugated and resonating hydrocarbons," *Trans. Faraday Soc.* **45**, 373–385 (1949).
- L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, 1966).
- I. Gutman, "Bounds for reactivity indices," *Theor. Chim. Acta* **47**, 217–222 (1978).
- E. Bright Wilson, Jr., "Obituary: Prof. William Moffitt," *Nature* **184**, 21–22 (1959).
- S. Altmann and E. Bowen, "Charles Alfred Coulson," *Biogr. Mem. Fellows R. Soc.* **20**, 74–134 (1974).
- R. Gregory and J. Murrell, "Christopher Longuet-Higgins. 11 April 1923–27 March 2004," *Biogr. Mem. Fellows R. Soc.* **52**, 149–166 (2006).
- C. Coulson, *Correspondence and Papers of Charles Alfred Coulson, FRS* (Bodleian Library, Oxford, 1974), Modern Manuscripts CSAC60.4.78, 175 boxes.
- I. Gutman and O. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer, Berlin, 1986).
- I. Sciriha, "A characterization of singular graphs," *Electron. J. Linear Algebra* **16**, 451–462 (2007).
- A. Brouwer and W. Haemers, *Spectra of Graphs*, Universitext (Springer, 2011).
- E. Braun, Y. Lee, S. Moosavi, S. Barthel, R. Mercado, I. Baburin, D. Proserpio, and B. Smit, "Generating carbon schwarzites via zeolite-templating," *Proc. Natl. Acad. Sci. U. S. A.* **115**, E8116–E8124 (2018).
- R. Haddon, " π -electrons in three dimensions," *Acc. Chem. Res.* **21**, 243–249 (1988).
- C. White and J. W. Mintmire, "Fundamental properties of single-wall carbon nanotubes," *J. Phys. Chem. B* **109**, 52–65 (2005).
- N. Hamada, S. Sawada, and A. Oshiyama, "New one-dimensional conductors: Graphitic microtubules," *Phys. Rev. Lett.* **68**, 1579–1581 (1992).