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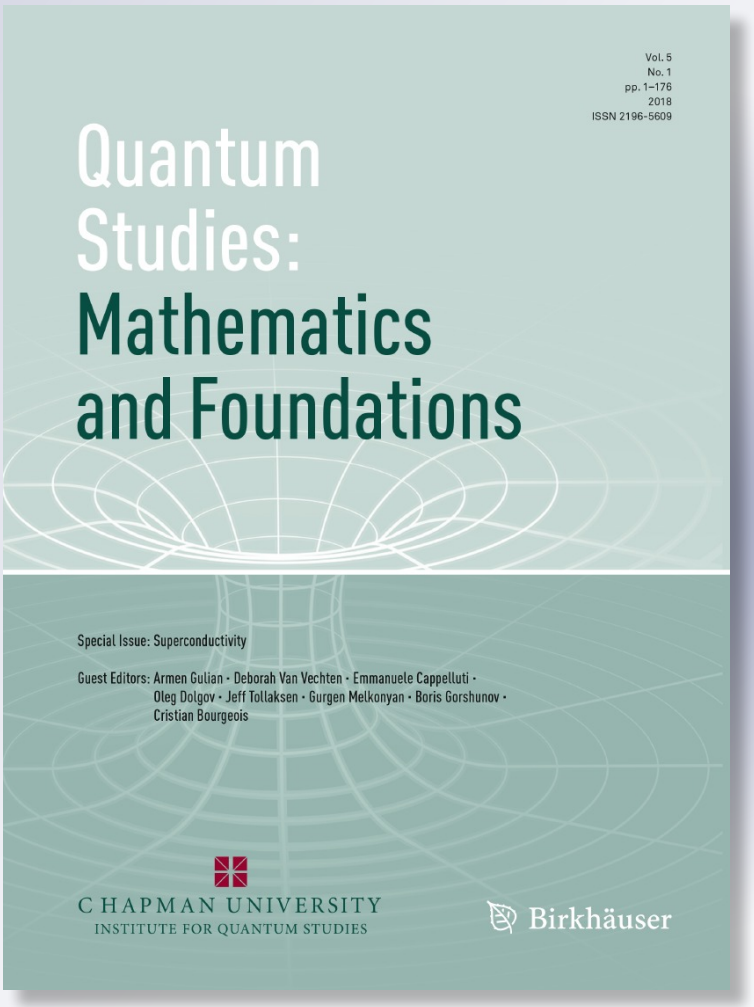

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REGULAR PAPER

Superconducting fluctuations in one-dimensional quasi-periodic "metallic" chains: the Little model of room-temperature superconductivity embodied

Paul M. Grant

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Abstract It is well known that a purely periodic chain of odd-electron atoms, nominally expected to exhibit metallic behavior, is unstable to charge/spin spatial displacement which lowers its ground-state energy by gapping its highly degenerate Jahn–Teller Fermi surface, in this case consisting of nesting parallel Brillouin zone sheets. It is largely for these reasons that superconductivity has not been observed in highly one-dimensional metals—it is simply energetically more favorable for CDW/SDW gaps to form, via chain dimerization, rather than a BCS state, at the very least one mediated by electron–phonon coupling. In this paper, we explore the hypothetical electronic properties of a nominally "metallic" quasi-periodic chain using both an analytical approach and computationally via density functional theory, searching for configurations which could possibly yield "gap-lets" sufficiently small to permit the formation of BCS pairs as the new energetically favored ground state. The particular embodiment we examine is a proxy structure consisting of a string of odd-electron atoms with interatomic spacing following a Fibonacci sequence, positioned above the surface of an appropriate highly polarizable material substrate. We propose a path to its computational modeling followed by a route to synthesis of such a structure for experimental examination, and thus perhaps leading to an entirely new class of near-room-temperature superconductors.

Keywords Room-temperature superconductors · Quasi-periodic metallic chain structures · Realizable Little models

1 Introduction

It is now slightly more than a century—and exactly 60 years—since the discovery of superconductivity in mercury metal by Gilles Holst in 1914 [1], to its explanation by Bardeen, Cooper and Schrieffer (aka "BCS") in 1957 [2]. Throughout all the years following, many refinements, both experimental and theoretical, to this remarkable phenomenon have taken place [3–7]. What has remained common and constant is that superconductivity, from millikelvin organic compounds to terakelvin neutron stars, results from a generalization of fermion pairing inevitably arising in a given boson field, as formulated within the BCS framework. In its simplest formulation, superconductivity can be described by,

$$T_C \sim \Theta \exp(-1/\lambda), \tag{1}$$

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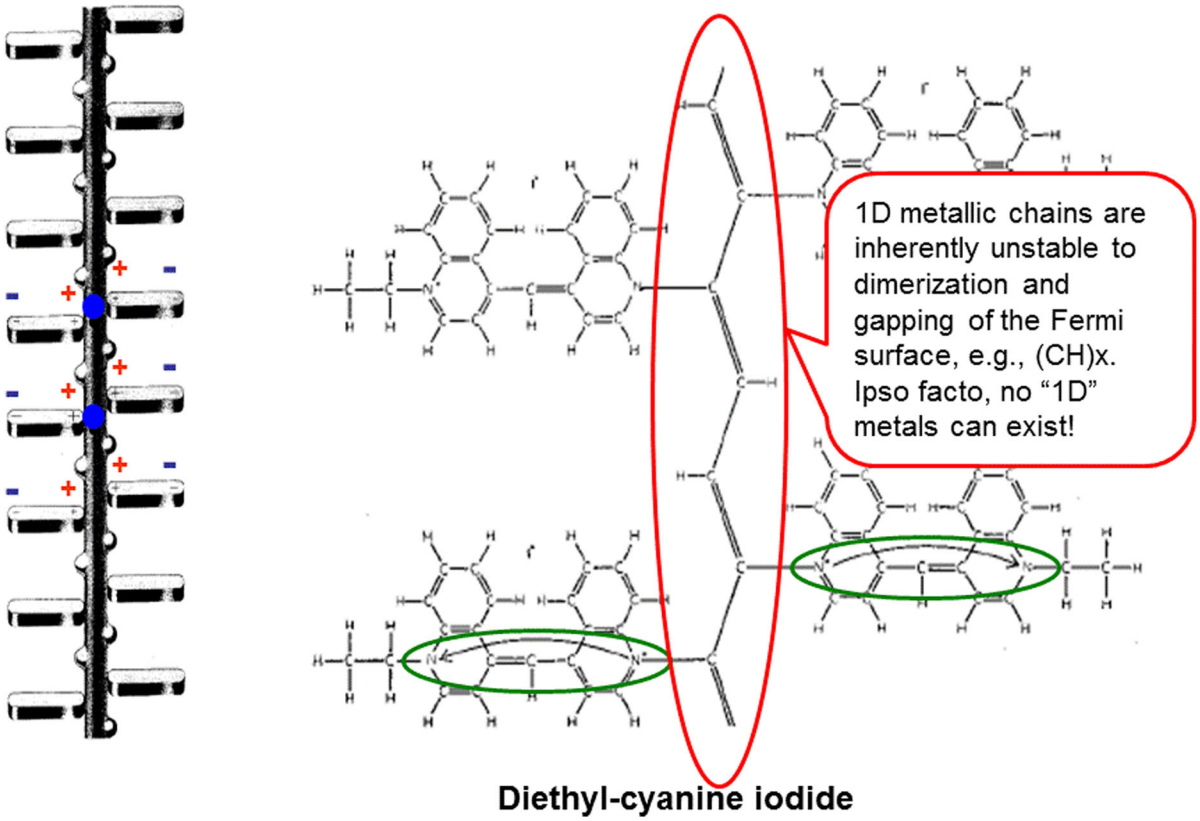

Fig. 1 Graphical summary of the original Little model (outlined in Refs. [8–11]). Central features are a dimerized polyacetylene ($(CH)_x$) chain (*red encircled*) surrounded by polarizable excitonic groups of diethyl-cyanine-iodide (polarizable component *green* enclosed). It is important to note that trans-polyacetylene has a band gap roughly 1–2 eV, requiring an exciton energy of at least that magnitude to effect pairing

where Θ is the characteristic energy of the boson field (usually proportional to the Debye temperature for a lattice of phonons), and λ the dimensionless coupling constant between the respective boson/fermion fields (e.g., the scattering of electrons in a simple metal brought on by "lattice shakings"). Typical computational values for basic metals, like Al (as obtained employing the Quantum Espresso package[1]), are T_C,s ranging from 0.9 to 2.0 K, λs $\sim$ 0.4 with Debye temperatures averaging 411 K. Not bad, given experimental values for Θ ranging from 390 to 433 K, and T_Cs $\sim$ 1.2 K!

Around 1964–1965, W. A. ("Bill") Little at Stanford University recognized that should the boson field be comprising excitons ($\Theta \approx$ 1–2 eV, or $\geq$12,000 K), the mediation of an even relatively weak electron–exciton coupling $\lambda \sim 0.5$, could result in a T_C well above room temperature (300 K) [8–11]. Little's conjecture encouraged other speculations as well, particularly by Allender et al. [12], a conjecture that remains controversial to the present day. One must remain aware, however, that the basis of the speculations surrounding references [8–12] were anticipated by Ginzburg [1] (search all references within, many of which were "unreachable" during the Cold War).

Little's basic idea is summarized in Fig. 1. Major features are a dimerized polyacetylene ($(CH)_x$) chain (red encircled) surrounded by polarizable excitonic groups of diethyl-cyanine-iodide (polarizable component green enclosed). It is important to note that trans-polyacetylene has a band gap roughly 1–2 eV, requiring an exciton

[1] All density functional calculations were performed using the open source Quantum Espresso package. Please visit the Quantum Espresso Web Page. For details regarding computations presented in Figs. 3, 4, please email w2agz@w2agz.com.

$$G_n \equiv G_{n-1} \,|\, G_{n-2}, \quad n = 3,4,5,\ldots,\infty$$

Where $G_1 = a,\ G_2 = ab$

And $\lim_{n\to\infty} N_a(G_n)/N_b(G_n) \equiv \tau = (1+\sqrt{5})/2 \approx 1.618\ldots$

Example: $G_6 = abaababaab$ $(N = 13)$

Let $a = c\tau b$, subject to $\langle a,b \rangle$ invariant,

And take a and b

to be "inter-atomic n-n distances,"

Then $b = \tau\langle a,b\rangle/[(1+c)\tau - 1]$.

Where c is a "scaling" parameter.

Fig. 2 Mathematical outline of a quasi-periodic sequence of Fibonacci numbers. *Note* that the $n = \infty$ limit of the ratio of the number of two possible sequential interatomic distances, a and b, is defined as a transcendental number, thus assuring quasi-periodicy

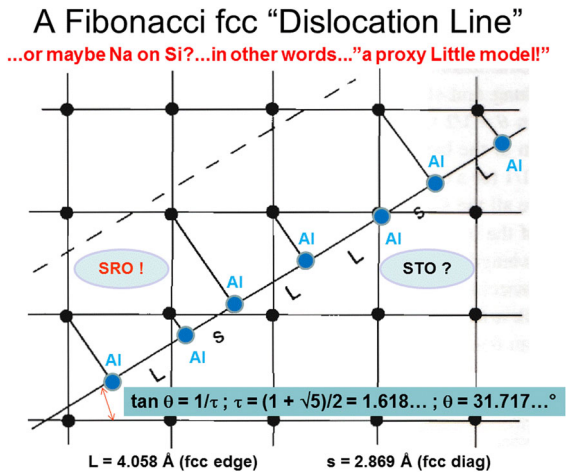

Fig. 3 One possible embodiment of a quasi-periodic sequence would be metallic Al atoms, deposited along a dislocation line, or "scratch", on the [001] surface of strontium ruthenate (SRO) or strontium titanate (STO) "decorated" by Al atoms. The efficacy of this embodiment needs to undergo study by appropriate DFT modeling prior to attempting fabrication

energy of at least that magnitude to effect pairing. Although fascinating, his model is structurally complex, and thus difficult to assess, even given present materials synthesis and computational tools.

In this paper, we undertake a description of a possible novel path involving computational DFT plus "response function" studies of feasible "proxy" structures perhaps achievable by emerging nano-fabrication technologies. We do this in the spirit of promoting a doctoral or post-doctoral effort at an appropriate institution. Pero, con quidado! Andale pues! Rough Mexican–American translation: "But watch out! Hurry up!". There is a preprint available from Physics Today published in 1998 [13] announcing its discovery in 2028 by the North American Physical Society!

2 A proxy structure embodiment of Little's vision

Thus, let us address a rather simple "proxy model" engendered mathematically by the Fibonacci "arithmetic" summarized in Fig. 2, and embodied by the Al atomic chain structure outlined in Fig. 3, where we imagine such a

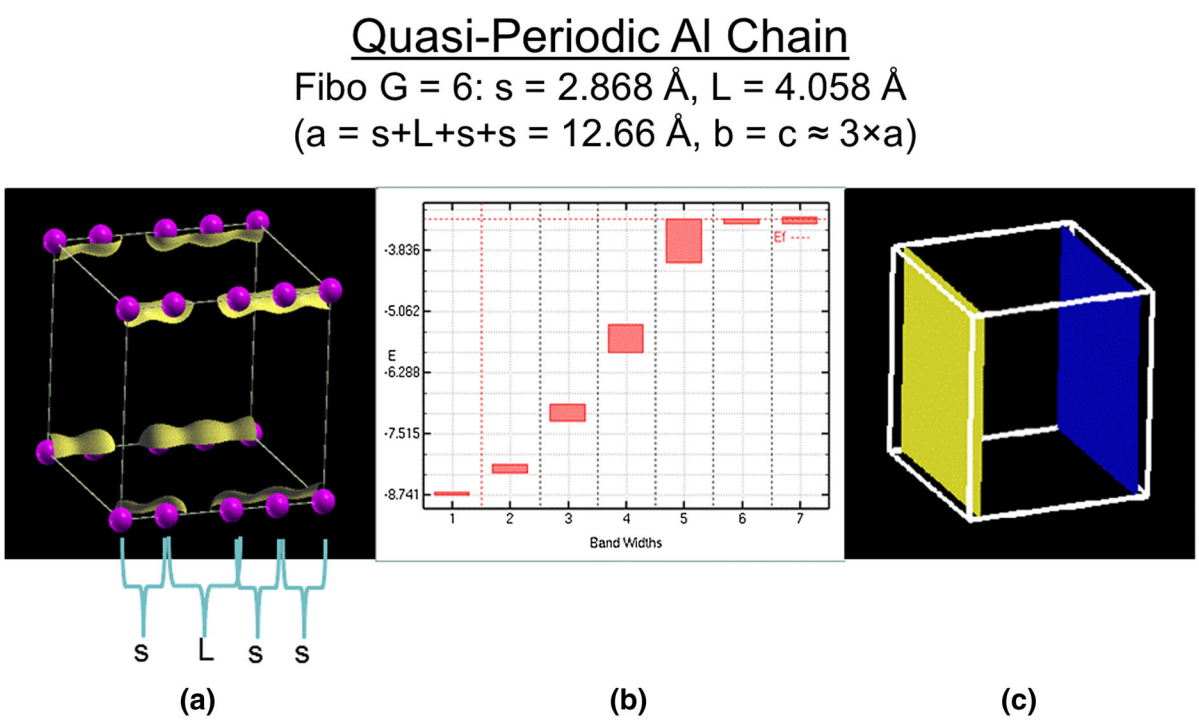

Fig. 4 Elementary DFT study of a "bare" Al chain as envisioned in Fig. 3 (see footnote 1). **a** The 3-D crystal structure of such a chain, with lattice parameters $b = c = 3a$ sufficiently separate to approximate its 1D nature. Note the nearest neighbor distances s and L are taken from the Fibonacci sequence postulated in Fig. 3, but the lattice constant for $a = s + L + s + s$ imposes an arbitrary periodicity required to perform a DFT calculation. The "yellow surfaces" depict an arbitrarily selected charge density resulting from the calculation. **b** Selected "mid-band energies" plotted as a function of band number, with the red bars reflecting total individual band widths. *Note* that the Fermi energy, E_f, passes through a very narrow band (7), thus imposing a small "metallicity". **c** The Fermi surfaces resulting from this weak metallic state are shown. In principle, this degeneracy would be removed by nesting as the a parameter increases by including more s and L units and approaches ideal quasi-periodicity. See body of text for further discussion

chain deposited along a lattice dislocation line, either "cracked" or "scratched" on the (001) face of a cubic perovskite crystalline substrate. Exactly how such a "proxy" could be realized remains in the imagination of the reader, but instinctively given the plethora of presently emerging epitaxial growth methods combined with nano-manipulation of atomic surface "decoration", all which are emerging as future tools of materials science, now live in the "inbox". Of course, it is important to keep in mind that it is only physically possible to approximate a truly Fibonacci chain, just as one can only approximate a transcendental number by a ratio of integers (recall being taught in the 4th grade that π is 22/7!), thus any practical realization of such a chain will certainly be periodic at some finite length.

This fact is made quite clear in Fig. 4 where we attempt a crude "band structure" calculation of a "quasi-periodic" Al string by imposing a threefold periodicity $s+L+s+s$ along the a-direction of a proxy cubic unit cell. Please see its caption for more details. The principle "take home" message is that increasing the length of the a lattice parameter following a Fibonacci sequence will not fundamentally result in a non-metallic state, but which would likely be eventually gapped by a small lattice distortion, but with a gap far smaller than that produced by dimerization as was the case of the trans-polyacetylene backbone chain of the classic Little model outlined in Fig. 1, and a gap easily bridged by excitons formed in a polarizable substrate (STO, SRO or Si), rather than at the more remote distance as would be the case for the cyanide side groups shown. As such, our model is perhaps more in line with the "Ginzburger" [5] or the metal–semiconductor interface proposed by Allender et al. [12].

Besides requiring a sound ground-state calculation, we also, and perhaps even more critically, must possess an inclusive response function from which to compute relevant superconducting properties, particularly T_C!

Davis – Gutfreund – Little (1975)

PHYSICAL REVIEW B VOLUME 13, NUMBER 11 1 JUNE 1976

Proposed model of a high-temperature excitonic superconductor*

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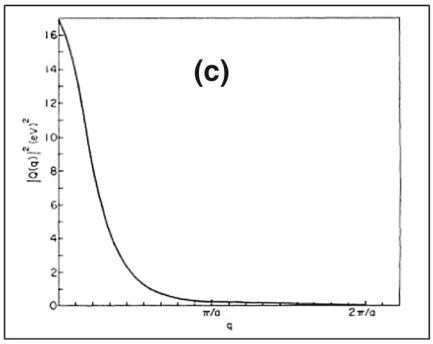
(Received 16 October 1975)

(a)

$$Q_\alpha(q) = \frac{1}{N^{3/2}} \int \sum_{j,k} \phi^*(r_1 - R_j)\,\phi(r_1 - R_h) e^{i[kR_h - (k-q)R_j]} V(r_1 r_2) \sum_{m,l,\nu} [u^\nu_{\alpha l}(q) + i v^\nu_{\alpha l}(q)]\, e^{-iqR_l}\, \Psi^*_\nu(R_{ml}) \Psi_{00}\, d^3r_1 d^3\tau$$



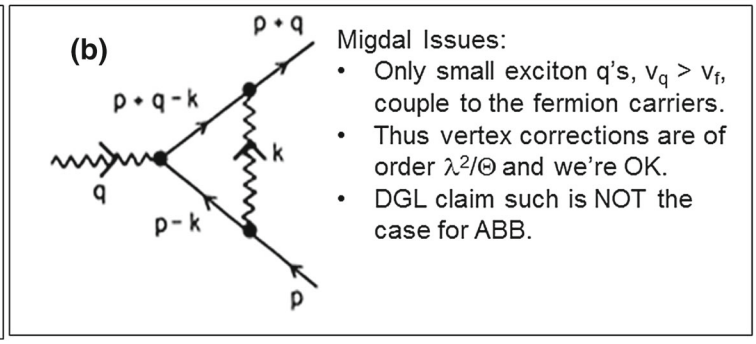


Fig. 5 All portions clipped and pasted from Ref. [11]. **a** Equation (23), a tight-binding approximation to the matrix element bonding adjacent "chains". The path forward is to "adjust" all for the present model. **b** Resolution of the Migdal issues relative to the Little model. **c** Dispersion of the relevant coupling boson strength vs. its quasi-momentum. *Note* the rather sharp "cutoff" and the connection to the distance "h" in Fig. 6 following

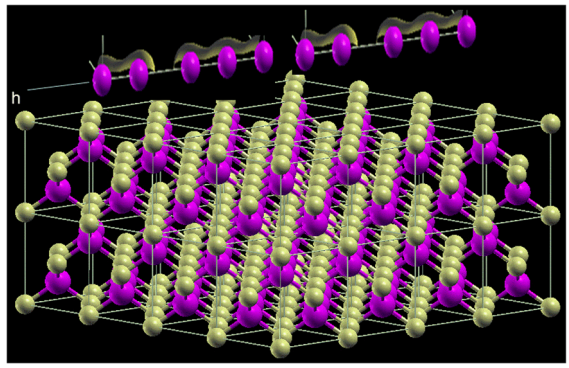


Fig. 6 A possible structural realization of the concepts presented in Figs. 3, 4. Shown is substrate consisting of the (001) surface of an otherwise single crystal of silicon, "decorated" along an appropriate quasi-periodic dislocation line with sodium, the latter positioned a distance "h" above that surface. Such could possibly be synthesized using AFM-derived "nano-derricks"

Such can be abstracted from Ref. [11], which follows on pioneer work by Kirschnitz et al. [6], perhaps the premier study focused on formulating a generalized dielectric function derived from an arbitrary basis set—just simply follow Eq. (24) in [11]. Much more algebraic manipulation is required for generalization to our quasi-periodic model string structure, but today the analytic path forward is straightforward, nevertheless tedious; see Fig. 5 and its caption.

Let us consider explicitly the structural model shown in Fig. 6, and as detailed in its caption, and then apply DFT followed by the calculation of Kirschnitz's dielectric constant, all as a function of the distance "h" from the Si (001) surface to the midline of the Na quasi-periodic chain, in the spirit of Fig. 3c. At what value of "h" is it necessary stay within in order to realize Little's vision as applied to this embodiment? Should our results show promise, how do we next fabricate a Fig. 6 reality? With today's rapidly expanding nano-fabrication toolbox, such structures might be possible employing AFM "nano-derricks!"

3 Conclusions

As stated earlier in Sect. 1, the purpose of the present paper is to propose a "proxy" approach to the realization of room-temperature superconductivity, via a simple computationally tractable structural model, as suggested in Figs. 3, 4 and 6, yet practically realizable via emerging nano-fabrication technology. The availability of a wide variety of DFT tools enables not only very accurate examination of the ground-state eigenfunctions of a given model, but also a variety of nearby excited states outside the reach of first- and second-order perturbation theory. The path to a general and appropriate "boson–fermion coupling" response function, an extension of the Kirschnitz et al., dielectric model [6], would next computationally be applied. Finally, should the model of Fig. 6, or similar structural proxies, prove promising, their nano-fabrication should be actively considered. As suggested in Sect. 1, a possible doctoral or post-doctoral undertaking indeed!

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